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General Chemistry: Atoms First

Chapter 11 Solutions and Their Properties

Lecture Notes

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Solutions

Solution: A homogeneous mixture of 2 or more components.

Solvent: The major component.

Solute(s): The minor component(s).

Solutions

TABLE 11.1 Some Different Kinds of Solutions

Kind of Solution	Example
Gas in gas	Air (O_2 , N_2 , Ar, and other gases)
Gas in liquid	Carbonated water (CO_2 in water)
Gas in solid	H_2 in palladium metal
Liquid in liquid	Gasoline (mixture of hydrocarbons)
Liquid in solid	Dental amalgam (mercury in silver)
Solid in liquid	Seawater (NaCl and other salts in water)
Solid in solid	Metal alloys, such as sterling silver (92.5% Ag, 7.5% Cu)

Divers for solution formation

$$\Delta G = \Delta H - T\Delta S$$

- *Enthalpy*
(ΔH)
- *Entropy*
(ΔS)

Divers for solution formation

$$\Delta G = \Delta H - T\Delta S$$

endothermic: $+\Delta H$

exothermic: $-\Delta H$

spontaneous: $-\Delta G$

non-spontaneous: $+\Delta G$

not favored: $-\Delta S$

favored: $+\Delta S$

Energy Changes and the Solution Process

$$\Delta G = \Delta H - T\Delta S$$

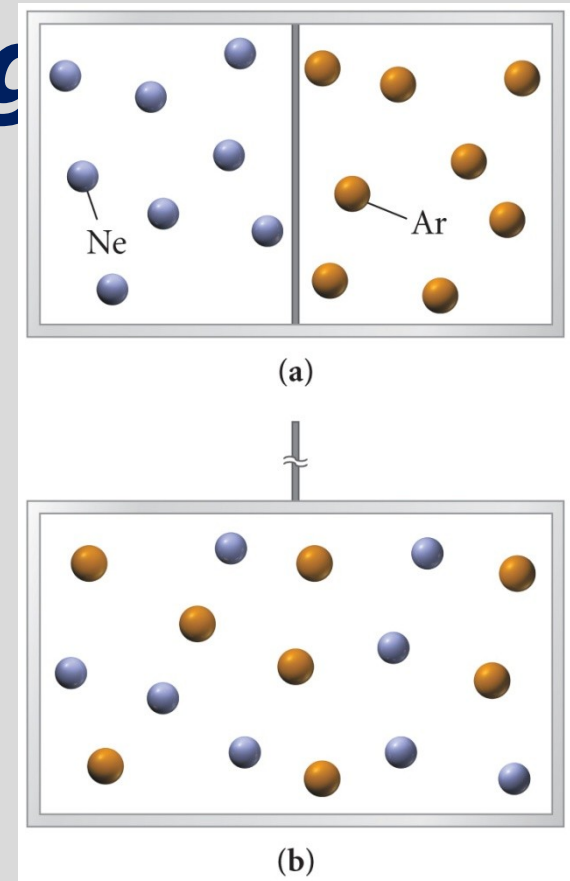
TABLE 11.2 Some Enthalpies and Entropies of Solution in Water at 25 °C

Substance	ΔH_{soln} (kJ/mol)	ΔS_{soln} [J/(K · mol)]
LiCl	−37.0	10.5
NaCl	3.9	43.4
KCl	17.2	75.0
LiBr	−48.8	21.5
NaBr	−0.6	54.6
KBr	19.9	89.0
KOH	−57.6	12.9

Mixing and the Solution Process

Entropy Change

- formation of a solution does not necessarily lower the potential energy of the system
 - the difference in attractive forces between atoms of two separate ideal gases vs. two mixed ideal gases is negligible
 - yet the gases mix spontaneously
- the gases mix because the energy of the system is lowered through the release of **entropy**
- **entropy** is the measure of energy dispersal throughout the system
- energy has a spontaneous drive to spread out over as large a volume as it is allowed



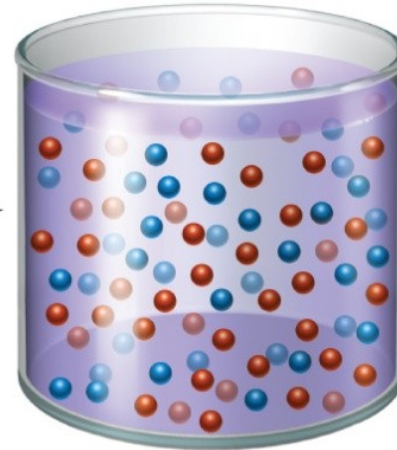
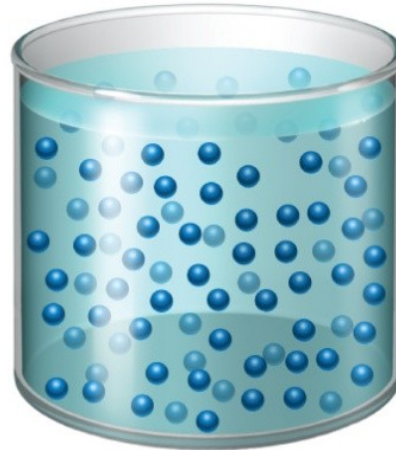
***Entropy* is one driver for creating a solution**

Less randomness
(less entropy)

More randomness
(more entropy)



+

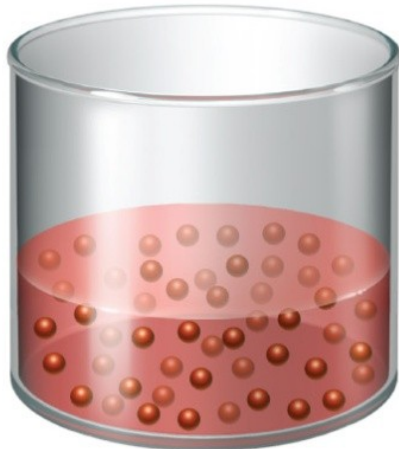


Solid

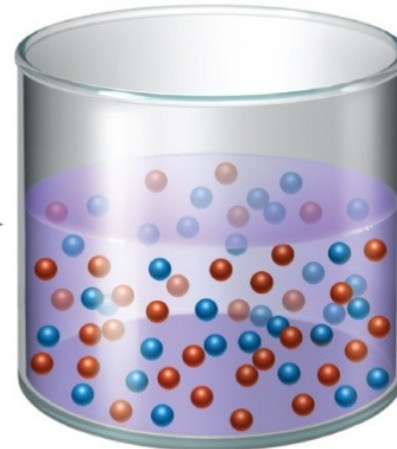
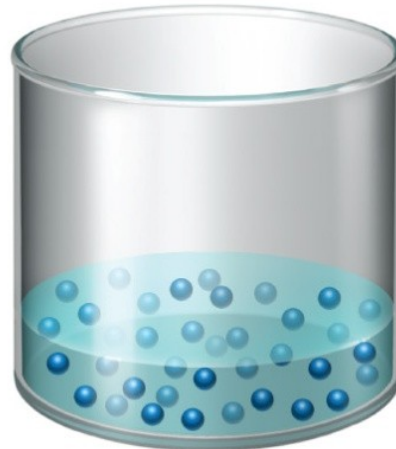
Liquid

Solution

Solution
#1



+



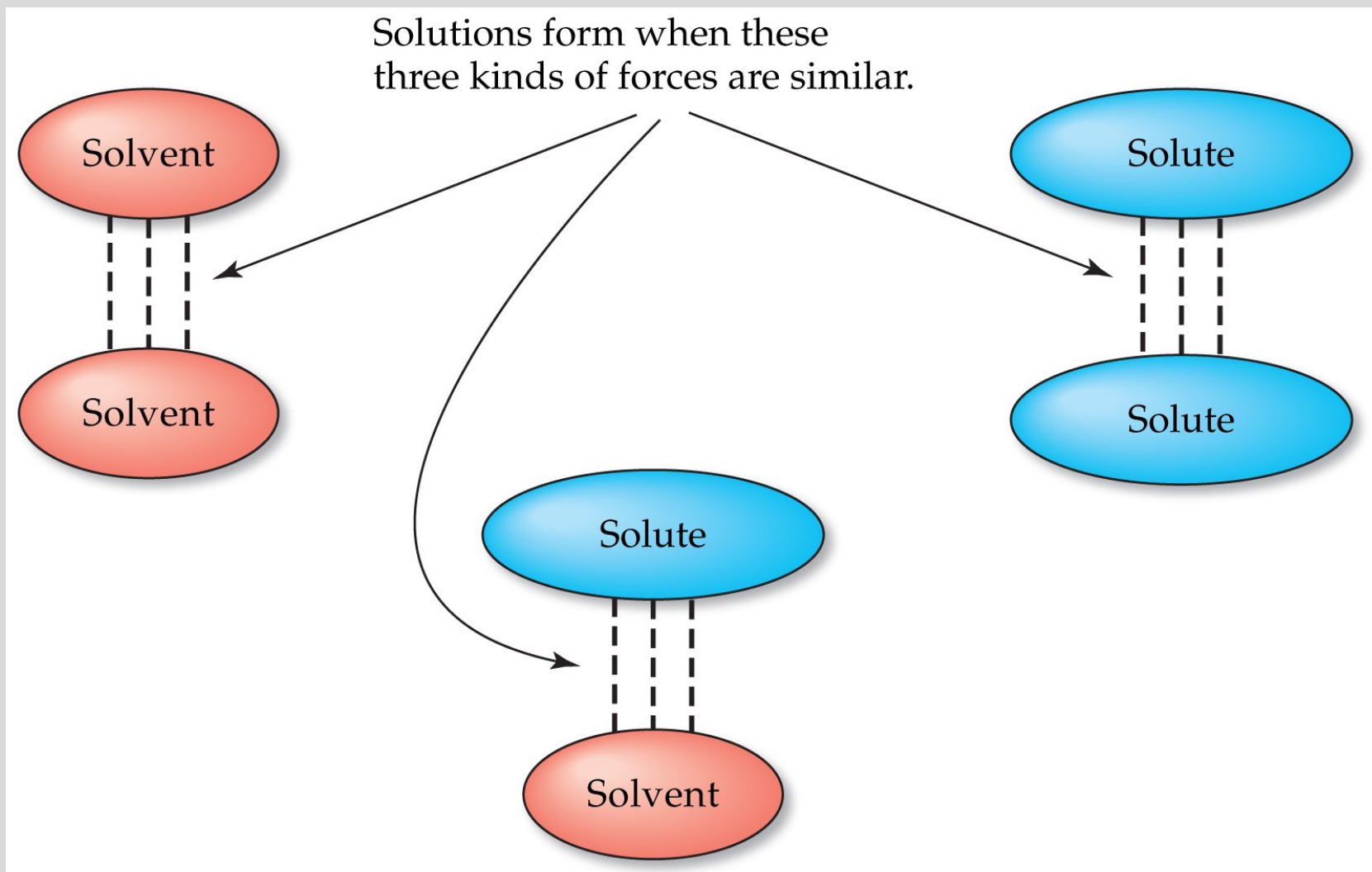
Liquid 1

Liquid 2

Solution

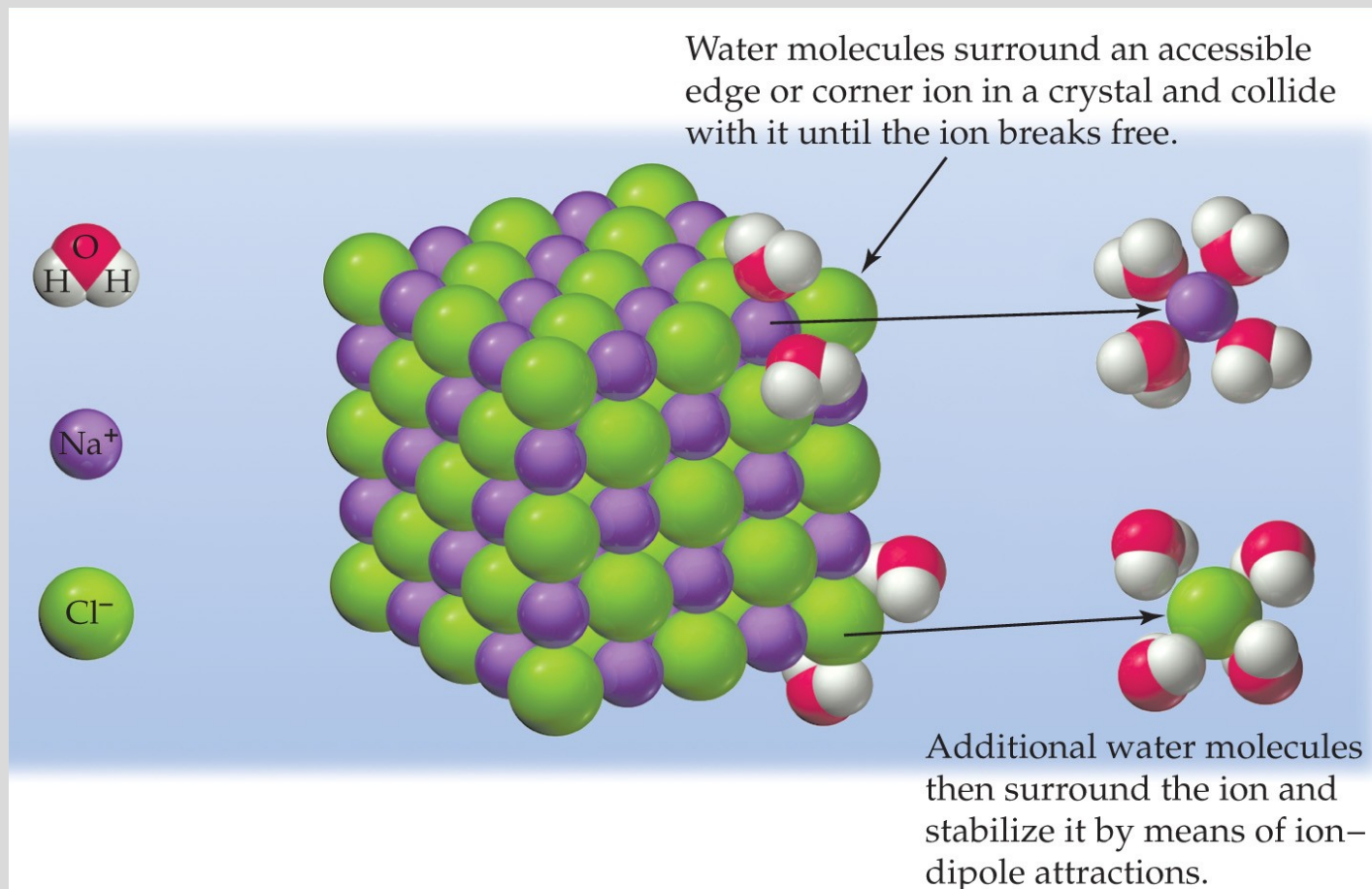
Solution
#2

Energy Changes and the Solution Process



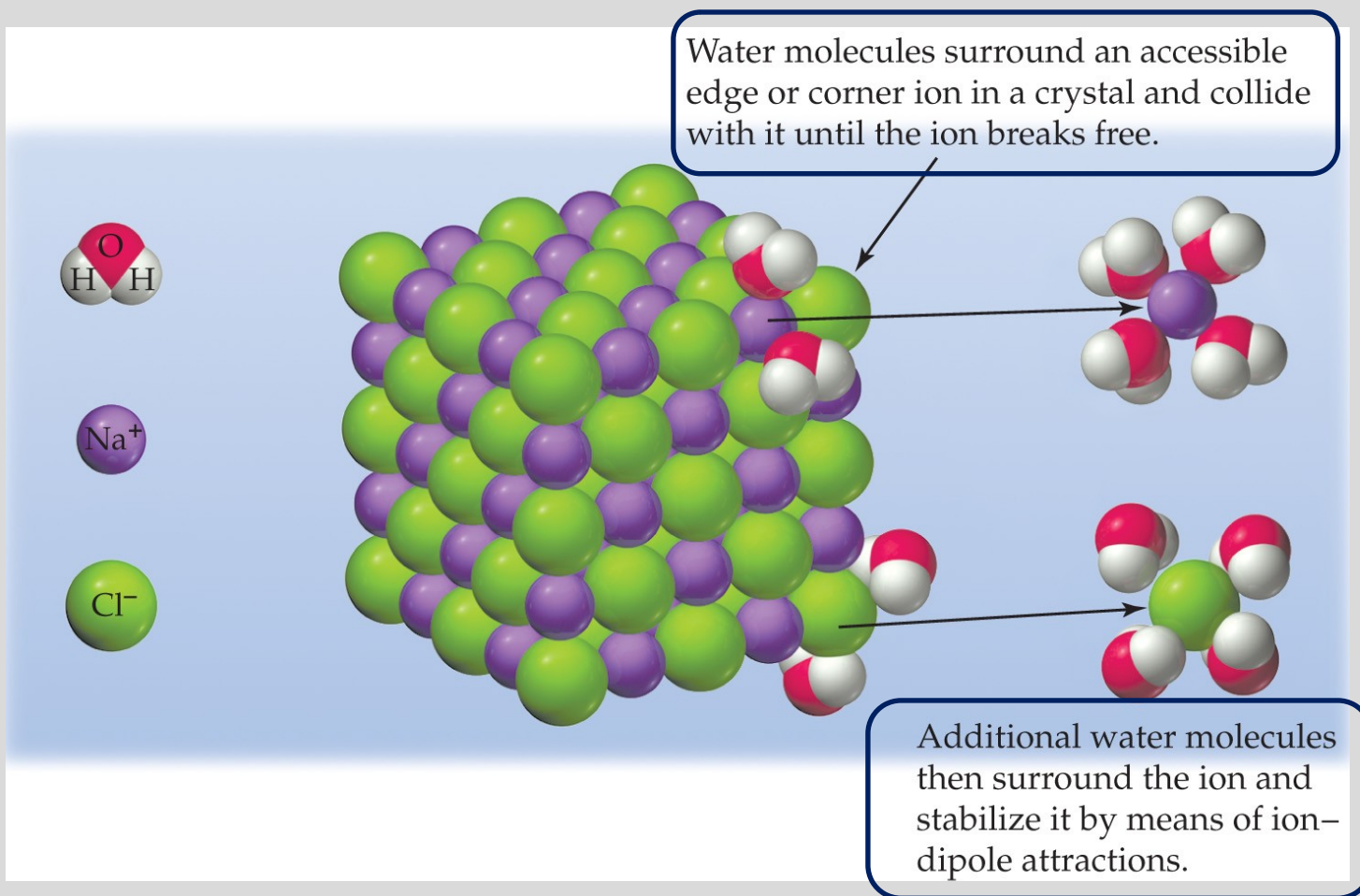
Energy Changes and the Solution Process

Dissolving Sodium Chloride in water, the sodium and chloride ions are *hydrated*.



Energy Changes and the Solution Process

There is an *entropy* change for the solution process.



Intermolecular Forces and the Solution Process - Enthalpy of Solution

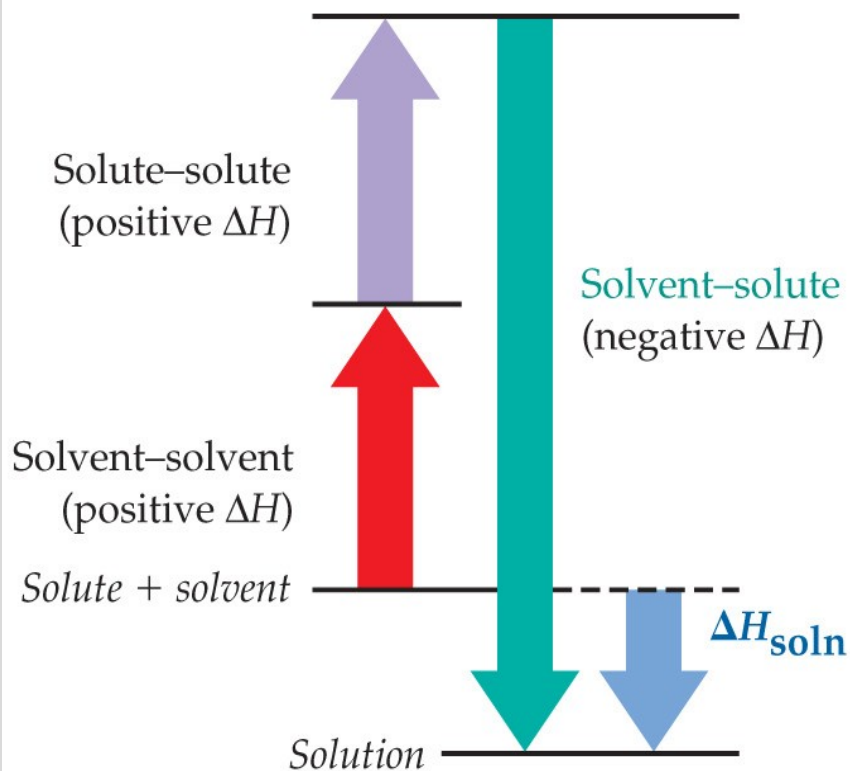
- energy changes resulting from the formation of most solutions involve differences in attractive forces between particles
- forming a solution must overcome both solute-solute and solvent-solvent attractive forces
 - both are endothermic
- at least some of the energy to do this comes from solute-solvent attractions
 - exothermic

Enthalpy Change for Solution Formation

- overcome attractions between
 - solute particles – **endothermic**
 - solvent molecules – **endothermic**
- attractions between solute particles and solvent molecules – **exothermic**
- the overall ΔH depends on the relative sizes of the ΔH for these 3 processes

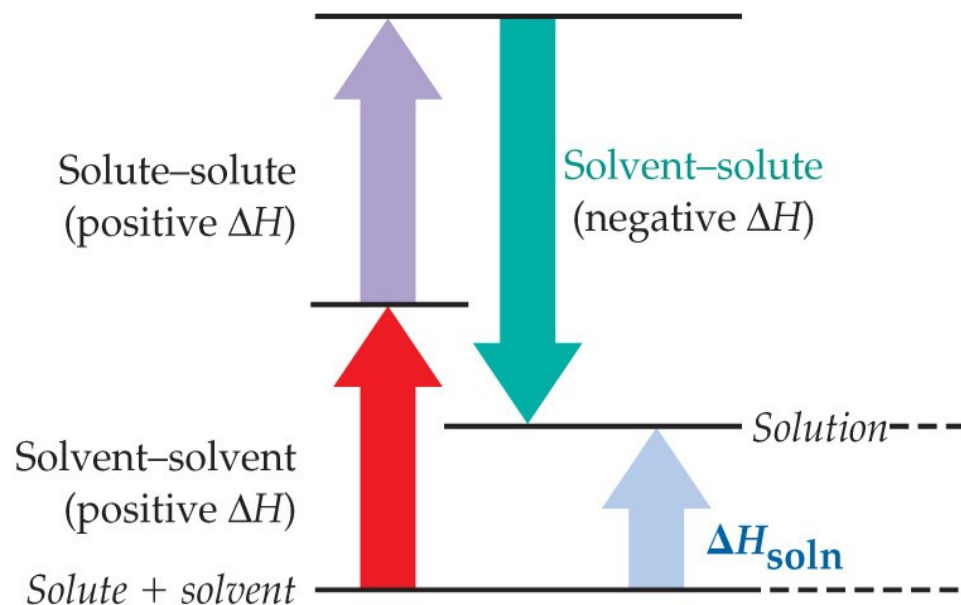
$$\Delta H_{\text{sol'n}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

Enthalpy Changes and the Solution Process



$$\Delta H_{\text{soln}} < 0$$

ΔH_{soln} is negative if solvent-solute interactions are dominant.



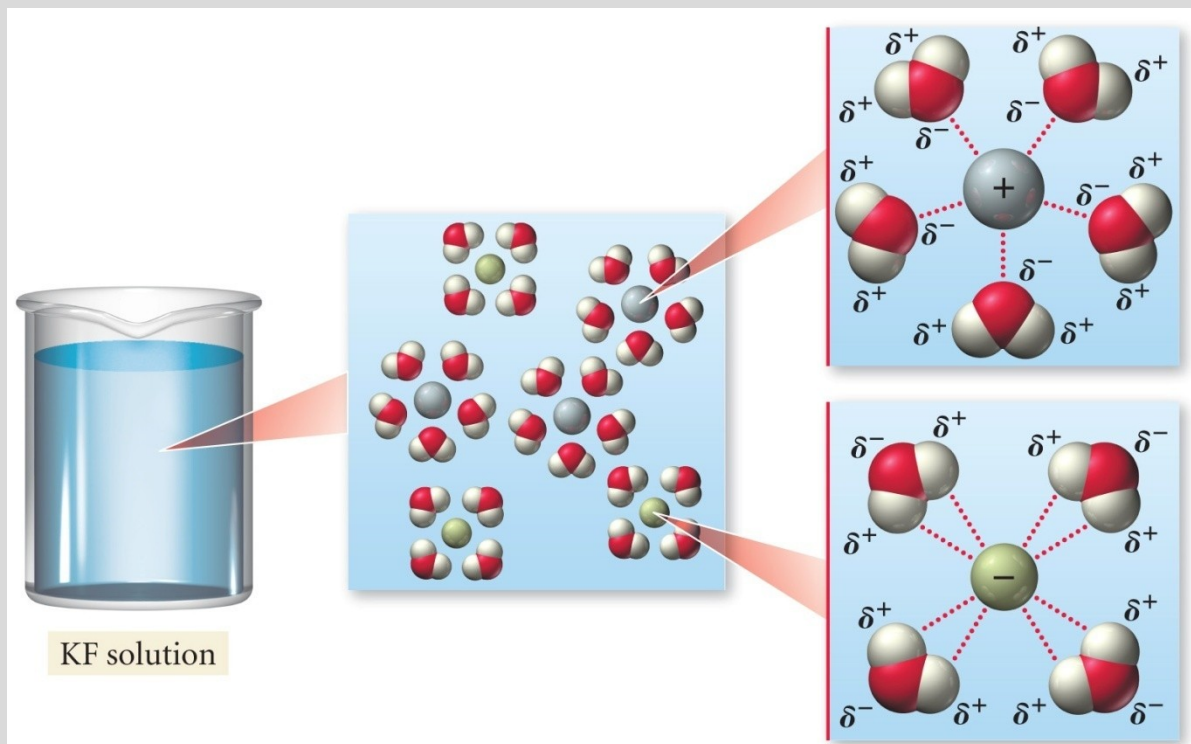
$$\Delta H_{\text{soln}} > 0$$

ΔH_{soln} is positive if solvent-solute interactions are not dominant.

Reasons for Enthalpy Changes

Ion-Dipole Interactions

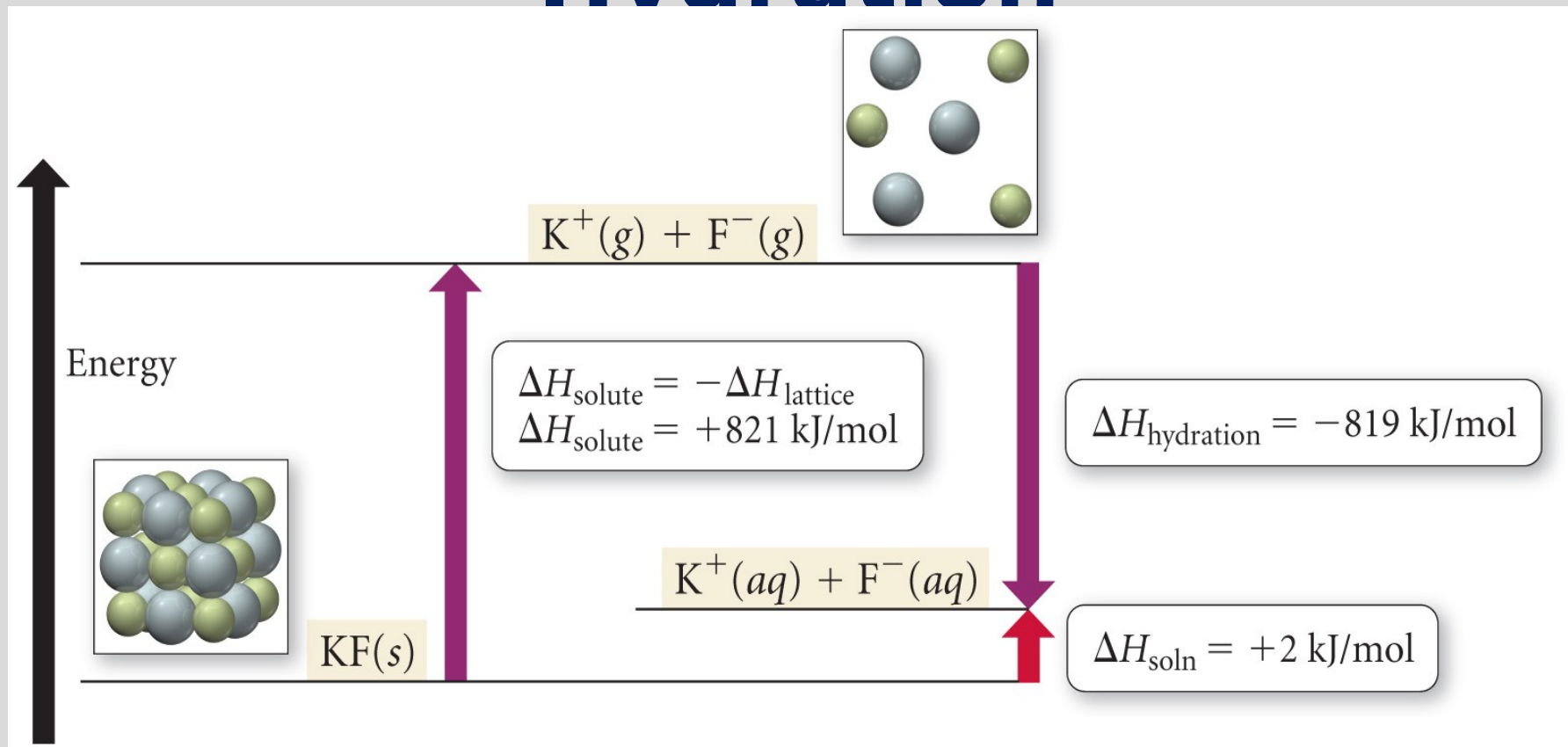
- when ions dissolve in water they become **hydrated**
- each ion is surrounded by water molecules



Reasons for Enthalpy Changes Heats of Hydration

- for aqueous ionic solutions, the energy added to overcome the attractions between water molecules and the energy released in forming attractions between the water molecules and ions is combined into a term called the **heat of hydration**
 - attractive forces in water = H-bonds
 - attractive forces between ion and water = ion-dipole
 - $\Delta H_{\text{hydration}}$ = heat released when 1 mole of gaseous ions dissolves in water

Reasons for Enthalpy Changes Heat of Hydration



Relative Interactions and Solution Formation

Solute-to-Solvent	>	Solute-to-Solute + Solvent-to-Solvent	Solution Forms
Solute-to-Solvent	=	Solute-to-Solute + Solvent-to-Solvent	Solution Forms
when the solute-to-solvent attractions are weaker than the sum of the solute-to-solute and solvent-to-solvent attractions, the solution will only form if the energy difference is small enough to be overcome by the entropy	<	Solute-to-Solute + Solvent-to-Solvent	May or May Not Form

Solubility

- when one substance (solute) dissolves in another (solvent) it is said to be **soluble**
 - salt is soluble in water
 - ethanol is soluble in water
 - bromine is soluble in methylene chloride
- when one substance does not dissolve in another it is said to be **insoluble**
 - oil is insoluble in water
- the solubility of one substance in another depends on two factors – nature's tendency towards mixing, and the types of inter-molecular attractive forces

Solubility

- there is usually a limit to the solubility of one substance in another
 - gases are ***always*** soluble in each other
 - two liquids that are mutually soluble are said to be **miscible**
 - alcohol and water are miscible
 - oil and water are immiscible
- the maximum amount of solute that can be dissolved in a given amount of solvent is called the **solubility**
- the solubility of one substance in another varies with temperature and pressure

Will It Dissolve?

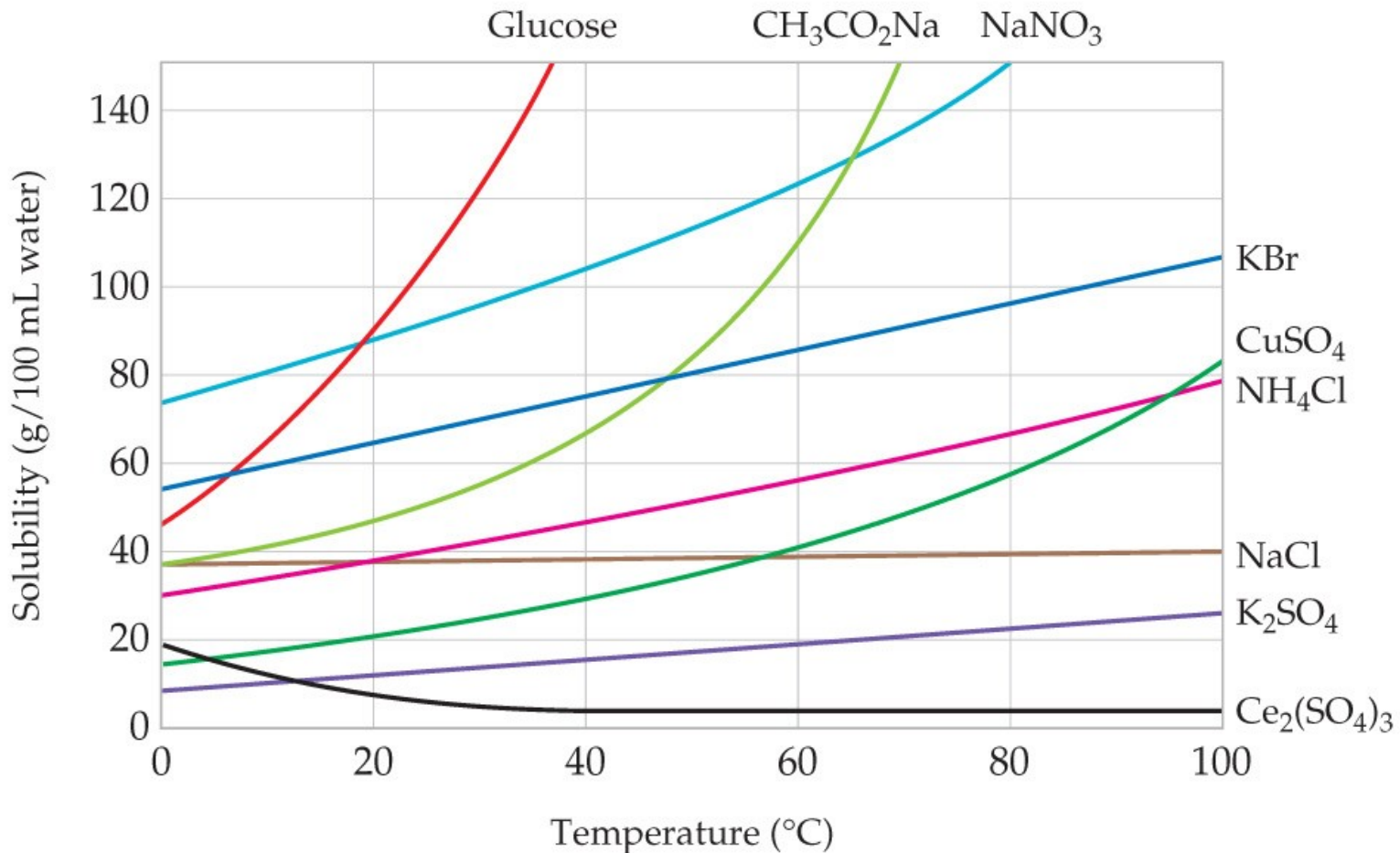
- Chemist's Rule of Thumb –

Like Dissolves Like

- a chemical will dissolve in a solvent if it has a similar structure to the solvent
- when the solvent and solute structures are similar, the solvent molecules will attract the solute particles at least as well as the solute particles to each other
 - polar and polar = soluble
 - non-polar and non-polar = soluble
 - polar and non-polar = insoluble

Some Factors Affecting Solubility

Most substances become more soluble as temperature increases, but the relationship between T and solubility is often complex & nonlinear



Classifying Solvents

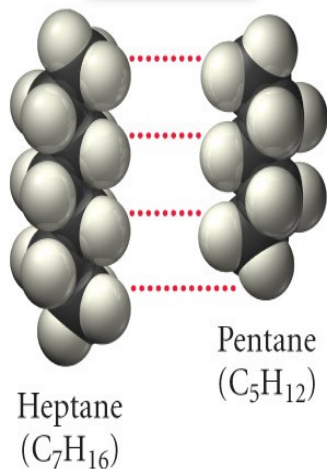
Solvent	Class	Structural Feature
Water, H ₂ O	polar	O-H
Methyl Alcohol, CH ₃ OH	polar	O-H
Ethyl Alcohol, C ₂ H ₅ OH	polar	O-H
Acetone, C ₃ H ₆ O	polar	C=O
Toluene, C ₇ H ₈	nonpolar	C-C & C-H
Hexane, C ₆ H ₁₄	nonpolar	C-C & C-H
Diethyl Ether, C ₄ H ₁₀ O	nonpolar	C-C, C-H & C-O, (nonpolar > polar)
Carbon Tetrachloride	nonpolar	C-Cl but

Intermolecular Attractions

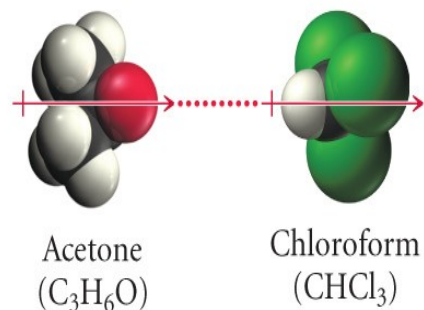
Intermolecular Forces

These forces may contribute to or oppose the formation of a solution.

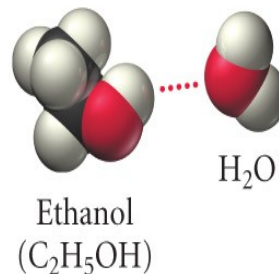
Dispersion



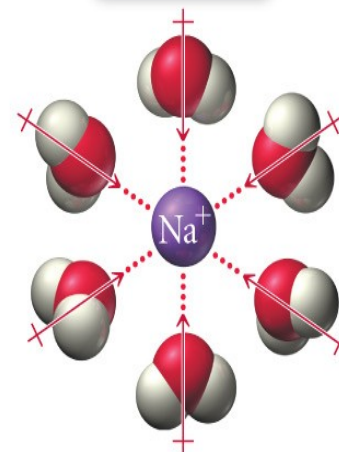
Dipole-dipole



Hydrogen bond



Ion-dipole

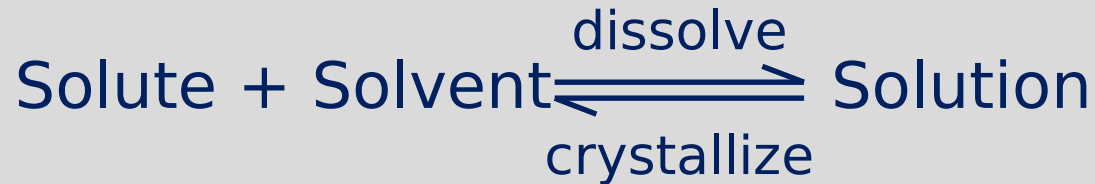


Solubility Limit

- a solution that has the maximum amount of solute dissolved in it is said to be **saturated**
 - depends on the amount of solvent
 - depends on the temperature
 - and pressure of gases
- a solution that has less solute than saturation is said to be **unsaturated**
- a solution that has more solute than saturation is said to be **supersaturated**

Some Factors Affecting Solubility

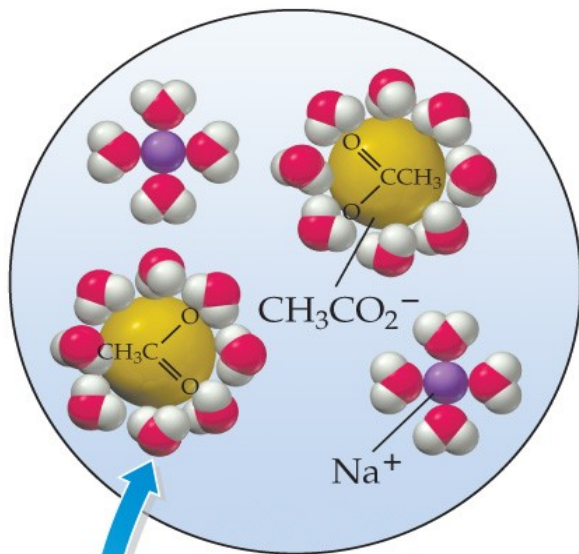
Saturated Solution: A solution containing the maximum possible amount of dissolved solute at equilibrium.



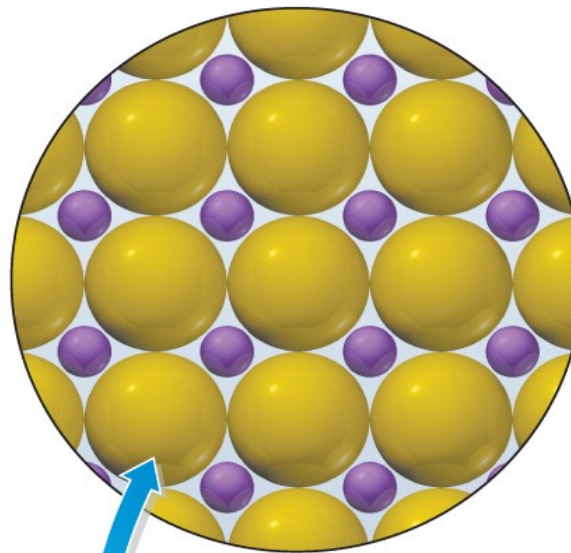
Supersaturated Solution: A solution containing a greater-than-equilibrium amount of solute.

How Can You Make a Solvent Hold More Solute Than It Is Able To?

- solutions can be made saturated at non-room conditions – then allowed to come to room conditions slowly
- for some solutes, instead of coming out of solution when the conditions change, they get stuck in-between the solvent molecules and the solution becomes supersaturated
- supersaturated solutions are unstable and lose all the solute above saturation when disturbed
 - e.g., shaking a carbonated beverage



A supersaturated solution of sodium acetate in water.



When a tiny seed crystal is added, larger crystals begin to grow and precipitate from the solution until equilibrium is reached.

Units of Concentration

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

$$\text{Mole Fraction (X)} = \frac{\text{Moles of component}}{\text{Total moles making up solution}}$$

$$\text{Mass Percent} = \frac{\text{Mass of component}}{\text{Total mass of solution}} \times 100\%$$

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

Units of Concentration

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

Assuming that seawater is an aqueous solution of NaCl, what is its molarity? The density of seawater is 1.025 g/mL at 20°C, and the NaCl concentration is 3.50 mass %.

Assuming 100.00 g of solution, calculate the volume:

$$100.00 \text{ g solution} \times \frac{1 \text{ mL}}{1.025 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.09756 \text{ L}$$

Convert the mass of NaCl to moles:

$$3.50 \text{ g NaCl} \times \frac{1 \text{ mol}}{58.4 \text{ g}} = 0.0599 \text{ mol}$$

Units of Concentration

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Liters of solution}}$$

Then, calculate the molarity:

$$\frac{0.0599 \text{ mol}}{0.09756 \text{ L}} = 0.614 \text{ M}$$

Units of Concentration

$$\text{Molality (} m \text{)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

What is the molality of a solution prepared by dissolving 0.385 g of cholesterol, $\text{C}_{27}\text{H}_{46}\text{O}$, in 40.0 g of chloroform, CHCl_3 ?

Convert the mass of cholesterol to moles:

$$0.385 \text{ g} \times \frac{1 \text{ mol}}{386.0 \text{ g}} = 0.000997 \text{ mol}$$

Calculate the mass of chloroform in kg:

$$40.0 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0400 \text{ kg}$$

Calculate the molality of the solution:

$$\frac{0.000997 \text{ mol}}{0.0400 \text{ kg}} = 0.0249 \text{ m}$$

Units of Concentration

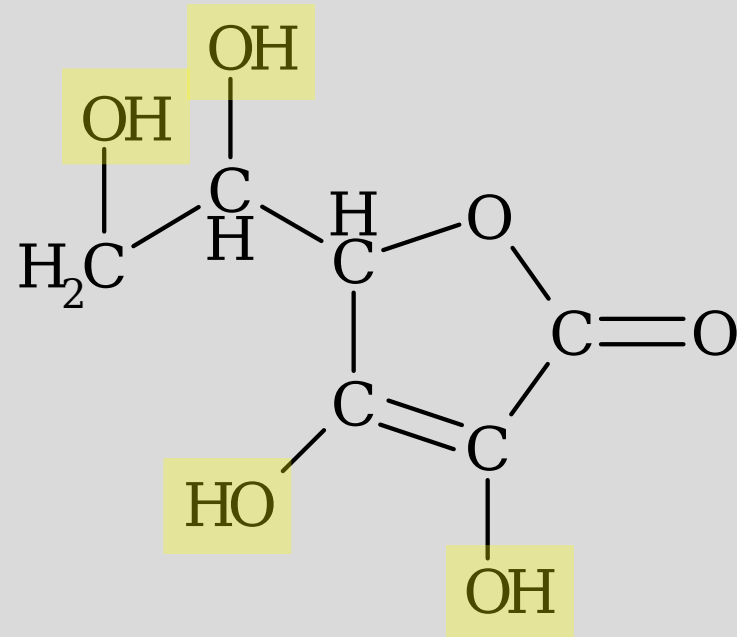
TABLE 11.3 A Comparison of Various Concentration Units

Name	Units	Advantages	Disadvantages
Molarity (M)	$\frac{\text{mol solute}}{\text{L solution}}$	Useful in stoichiometry; measure by volume	Temperature-dependent; must know density to find solvent mass
Mole fraction (X)	None	Temperature-independent; useful in special applications	Measure by mass; must know density to convert to molarity
Mass %	%	Temperature-independent; useful for small amounts	Measure by mass; must know density to convert to molarity
Molality (<i>m</i>)	$\frac{\text{mol solute}}{\text{kg solvent}}$	Temperature-independent; useful in special applications	Measure by mass; must know density to convert to molarity

Example - predict whether the following vitamin is soluble in fat or water

The 4 OH groups make the molecule highly polar and it will also H-bond to water.

Vitamin C is water soluble

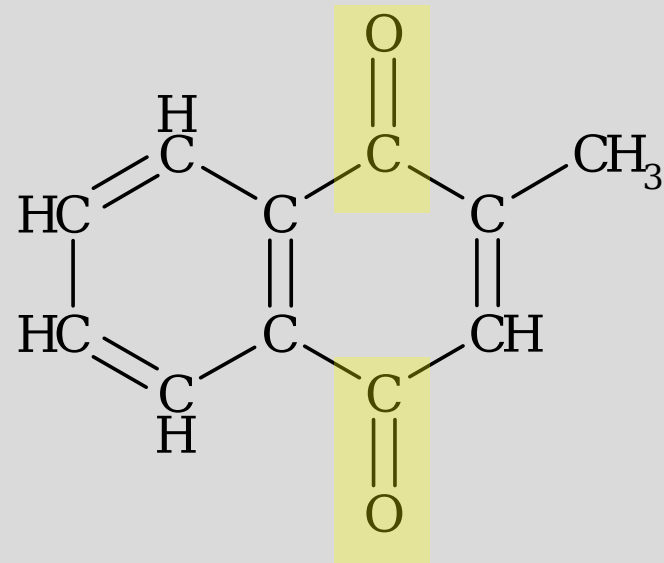


Vitamin C

Example - predict whether the following vitamin is soluble in fat or water

The 2 C=O groups are polar, but their geometric symmetry suggests their pulls will cancel and the molecule will be non-polar.

Vitamin K₃ is fat soluble



Vitamin K₃

Ideal vs. non-ideal Solution

- in ideal solutions, the solute-solvent interactions created are equal to the sum of the broken solute-solute and solvent-solvent interactions
 - ideal solutions follow Raoult's Law
- effectively, the solute is diluting the solvent
- **if the solute-solvent interactions are stronger or weaker than the solute-solute and the solvent-solvent interactions the solution is non-ideal**

Non-ideal Solution Vapor Pressure

- when the **solute-solvent interactions** are **stronger** than the solute-solute + solvent-solvent, the **total vapor pressure of the solution will be less** than predicted by Raoult's Law
 - because the vapor pressures of the solute and solvent are lower than ideal
- when the **solute-solvent interactions** are **weaker** than the solute-solute + solvent-solvent, the **total vapor pressure of the solution will be larger** than predicted by Raoult's Law

Freezing Point Depression

- the freezing point of a solution is lower than the freezing point of the pure solvent
 - for a nonvolatile solute
 - therefore the melting point of the solid solution is lower
- the difference between the freezing point of the solution and freezing point of the pure solvent is directly proportional to the molal (moles/kg) concentration of solute particles
- $(FP_{\text{solvent}} - FP_{\text{solution}}) = \Delta T_f = m \cdot K_f$
the proportionality constant is called the Freezing Point Depression Constant, K_f
 - ✓ the value of K_f depends on the solvent
 - ✓ the units of K_f are $^{\circ}\text{C}/m$

Colligative Properties

- **colligative properties** are properties whose value depends only on the number of solute particles, and not on what they are
 - Vapor-Pressure Lowering
 - Boiling-Point Elevation
 - Freezing-Point Depression
 - Osmotic Pressure

the **van't Hoff factor, i** , is the ratio of moles of solute particles to moles of formula units dissolved

measured van't Hoff factors are often lower than you might expect due to ion pairing in solution

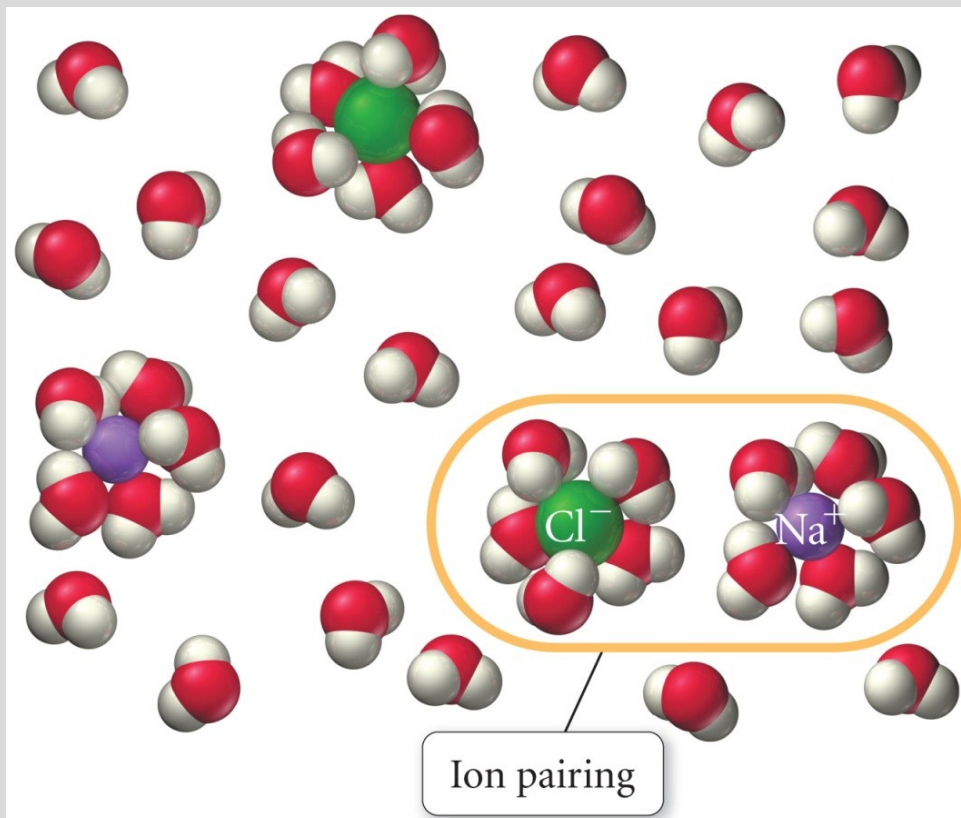


TABLE 12.9 Van't Hoff Factors at 0.05 *m* Concentration in Aqueous Solution

Solute	<i>i</i> Expected	<i>i</i> Measured
Nonelectrolyte	1	1
NaCl	2	1.9
MgSO ₄	2	1.3
MgCl ₂	3	2.7
K ₂ SO ₄	3	2.6
FeCl ₃	4	3.4

TABLE 12.8 Freezing Point Depression and Boiling Point Elevation Constants for Several Liquid Solvents

Solvent	Normal Freezing Point ($^{\circ}\text{C}$)	$K_f(^{\circ}\text{C}/m)$	Normal Boiling Point ($^{\circ}\text{C}$)	$K_b(^{\circ}\text{C}/m)$
Benzene (C_6H_6)	5.5	5.12	80.1	2.53
Carbon tetrachloride (CCl_4)	-22.9	29.9	76.7	5.03
Chloroform (CHCl_3)	-63.5	4.70	61.2	3.63
Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	-114.1	1.99	78.3	1.22
Diethyl ether ($\text{C}_4\text{H}_{10}\text{O}$)	-116.3	1.79	34.6	2.02
Water (H_2O)	0.00	1.86	100.0	0.512

Boiling Point Elevation

- the boiling point of a solution is higher than the boiling point of the pure solvent
 - for a nonvolatile solute
- the difference between the boiling point of the solution and boiling point of the pure solvent is directly proportional to the molal concentration of solute particles

$$(\text{BP}_{\text{solution}} - \text{BP}_{\text{solvent}}) = \Delta T_b = m \cdot K_b$$

- the proportionality constant is called the Boiling Point Elevation Constant, K_b
 - the value of K_b depends on the solvent
 - the units of K_b are $^{\circ}\text{C}/m$

Solution Equilibrium

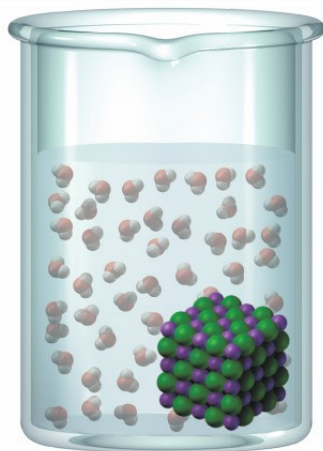
- the dissolution of a solute in a solvent is an equilibrium process
- initially, when there is no dissolved solute, the only process possible is dissolution
- shortly, solute molecules can start to recombine to reform solute particles – but the rate of dissolution $\gg$ rate of deposition and the solute continues to dissolve
- eventually, the rate of dissolution = the rate of deposition – the solution is saturated with solute and no more solute will dissolve

Solution Equilibrium

Solution Equilibrium



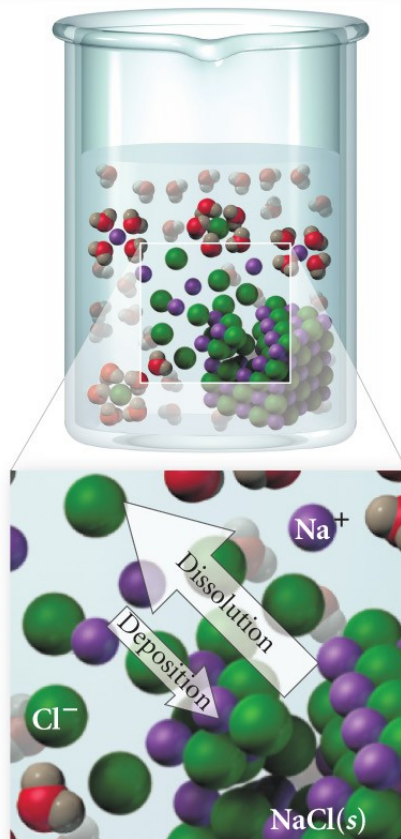
When sodium chloride is first added to water, sodium and chloride ions begin to dissolve into the water.



(a) Initial



As the solution becomes more concentrated, some of the sodium and chloride ions can begin to redeposit as solid sodium chloride.

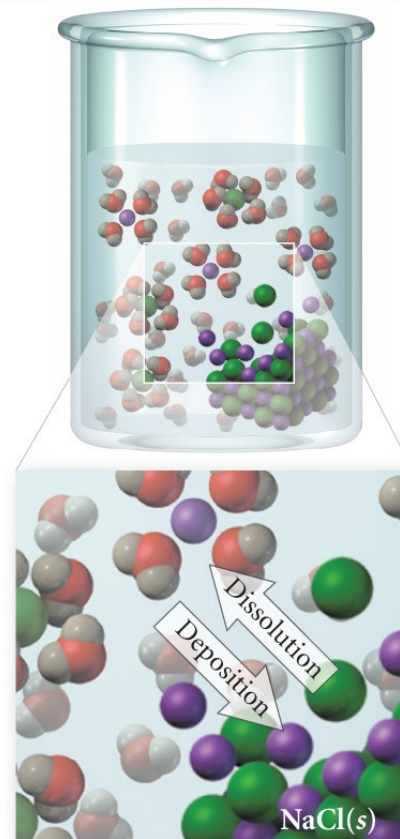


Rate of dissolution > Rate of deposition

(b) Dissolving



When the rate of dissolution equals the rate of deposition, dynamic equilibrium has been reached.



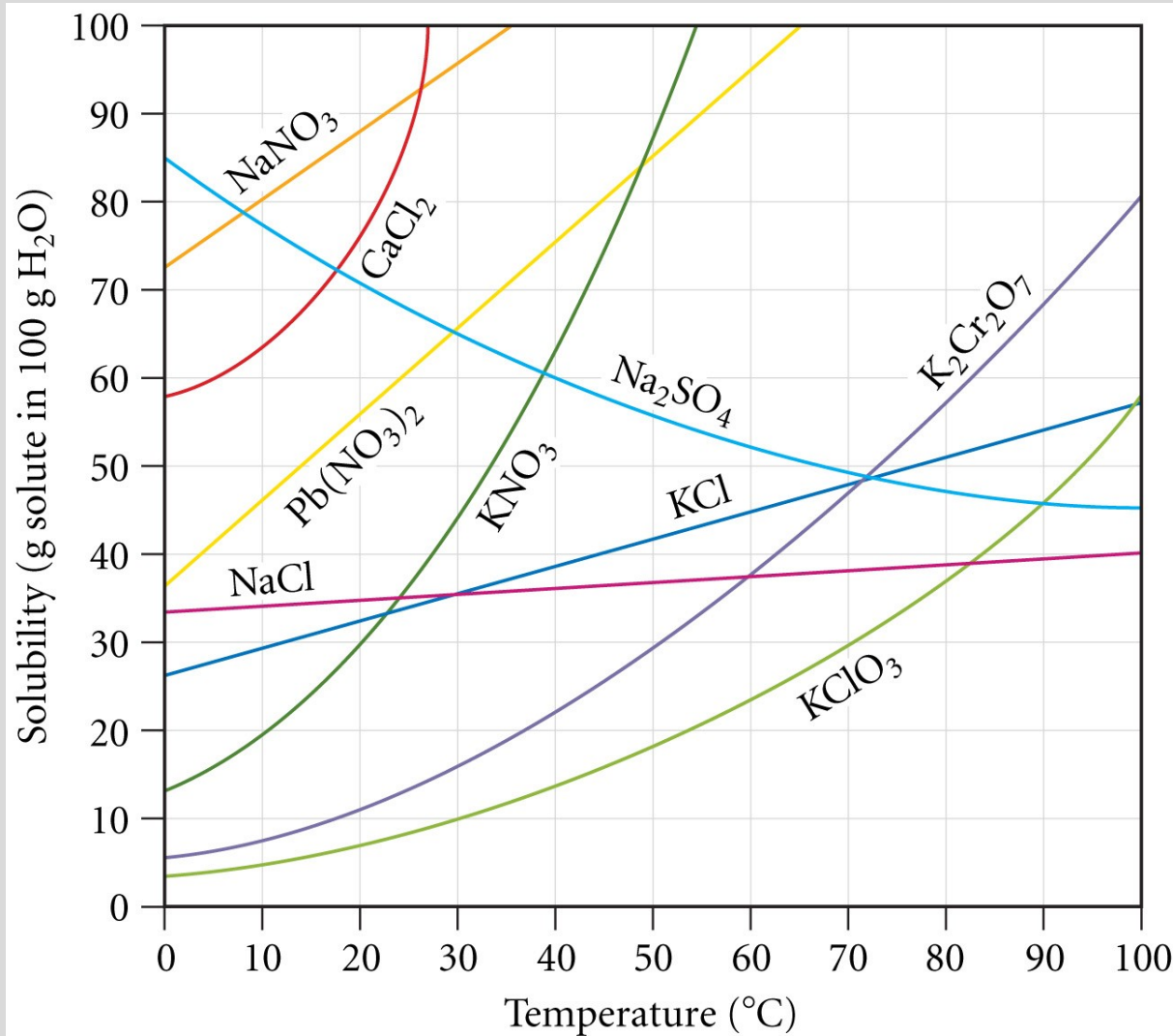
Rate of dissolution = Rate of deposition

(c) Dynamic equilibrium

Temperature Dependence of Solubility of Solids in Water

- solubility is generally given in grams of solute that will dissolve in 100 g of water
- for **most** solids, the solubility of the solid increases as the temperature increases
 - when $\Delta H_{\text{solution}}$ is endothermic

Solubility Curves

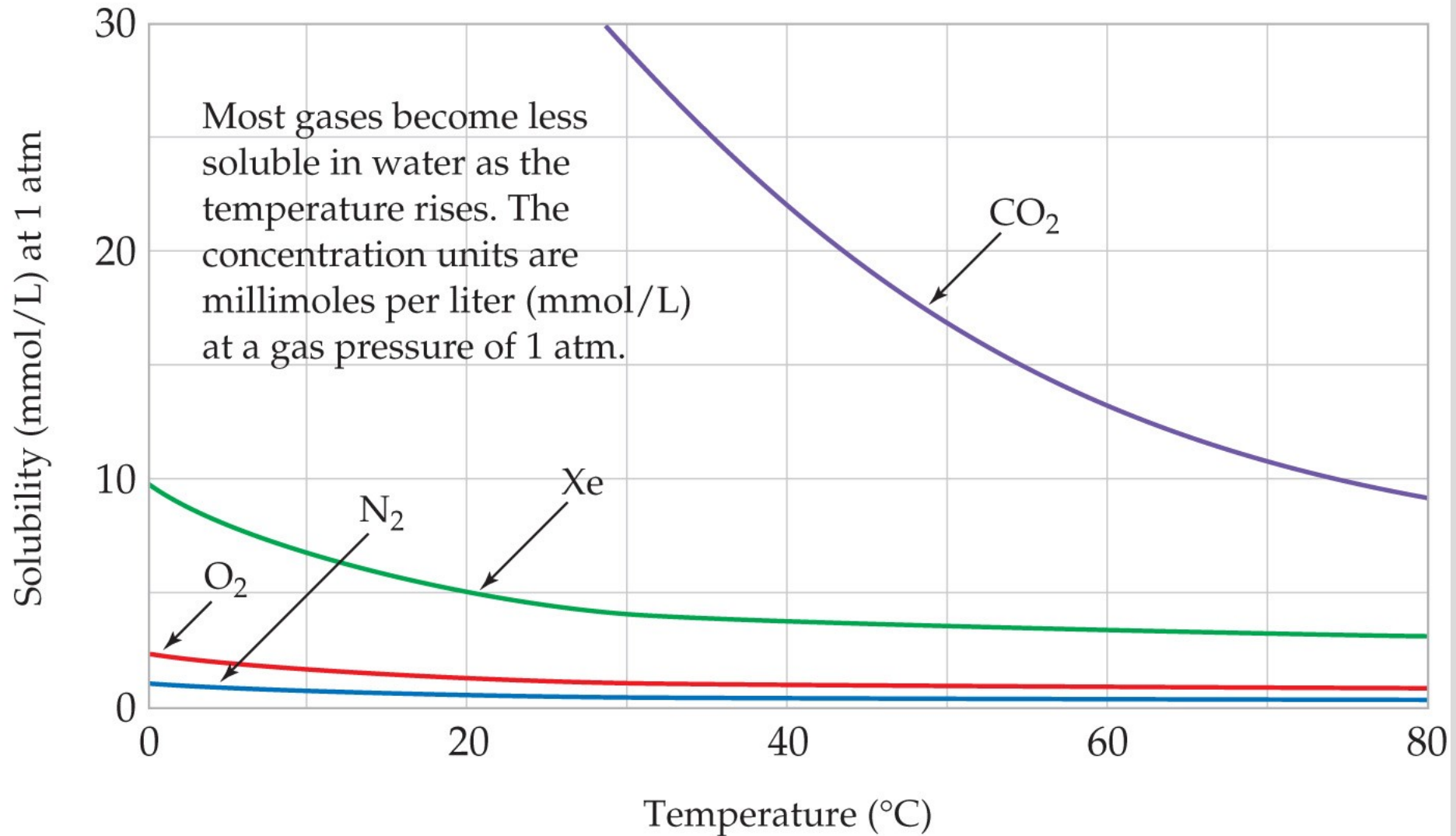


solubility curves
can be used to
predict whether
a solution with
a particular
amount of
solute dissolved
in water is
saturated (on
the line),
unsaturated
(below the line),
or
supersaturated
(above the
line)

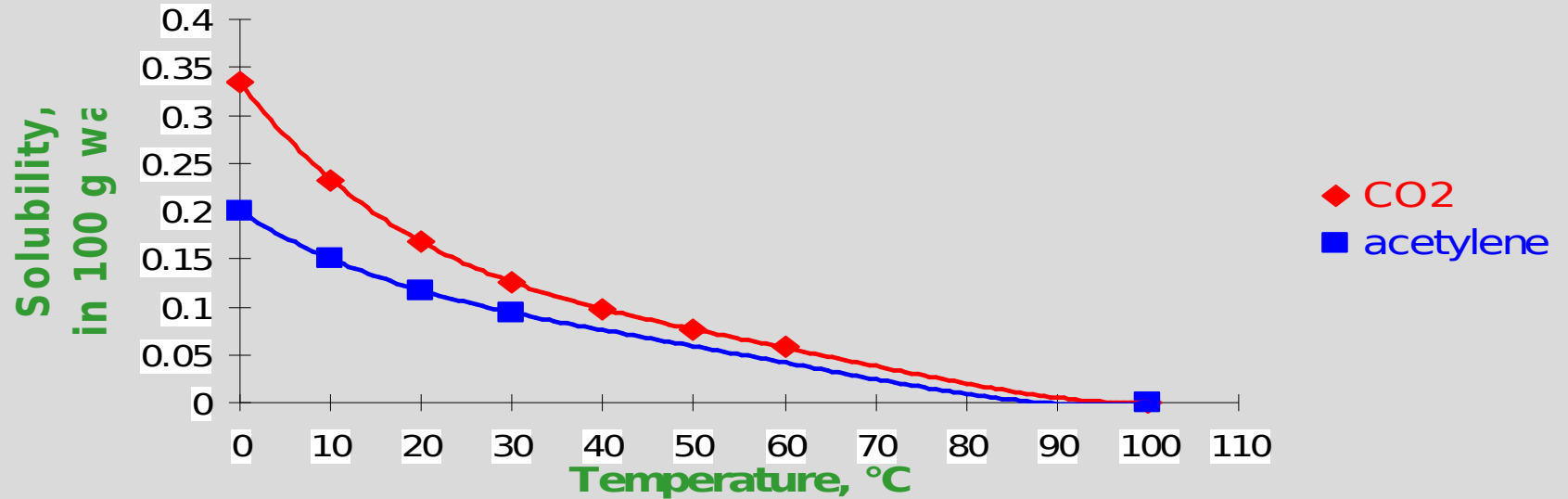
Temperature Dependence of Solubility of Gases in Water

- for **all** gases, the solubility of the gas decreases as the temperature increases
 - the $\Delta H_{\text{solution}}$ is exothermic because you don't need to overcome solute-solute attractions
- Solubility can also be given in moles of solute that will dissolve in 1 Liter of solution
- generally gases have lower solubility than ionic or polar covalent solids because most are nonpolar molecules

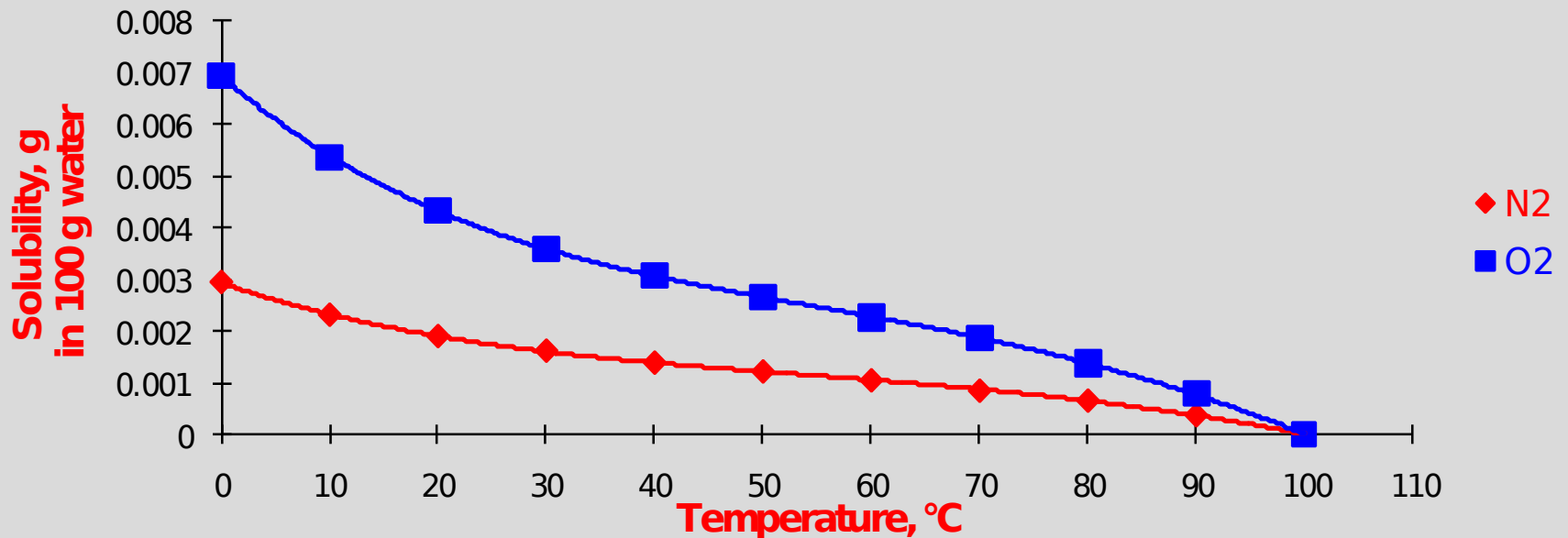
Gas Solubility vs. Temperature



Solubility of Gases in Water at Various Temperatures

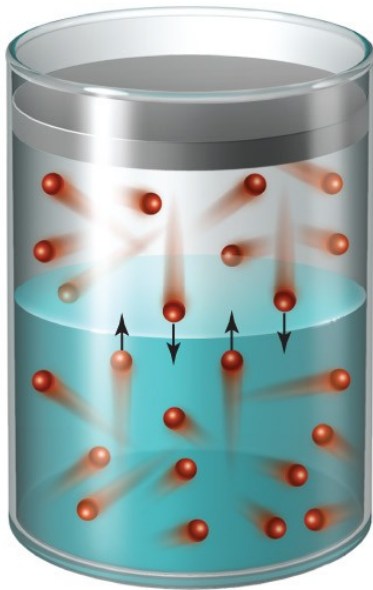


Solubility of Gases in Water at Various Temperatures



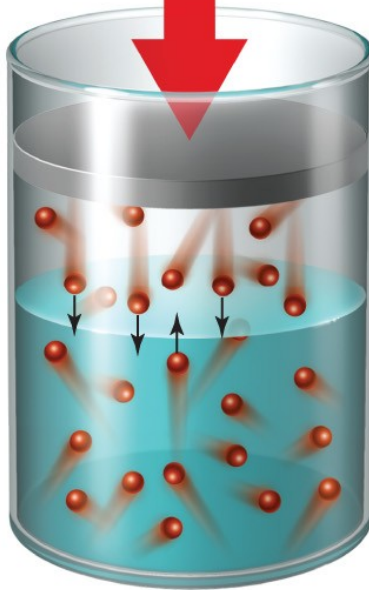
Some Factors Affecting Henry's Law Solubility

Solubility = $k P$



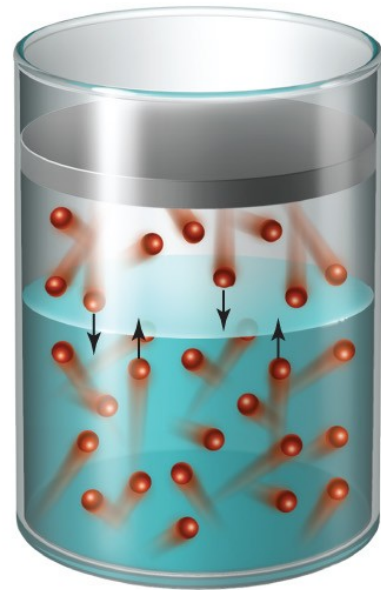
Equilibrium

At a given pressure, an **equilibrium** exists in which equal numbers of gas particles enter and leave the solution.



Pressure increase

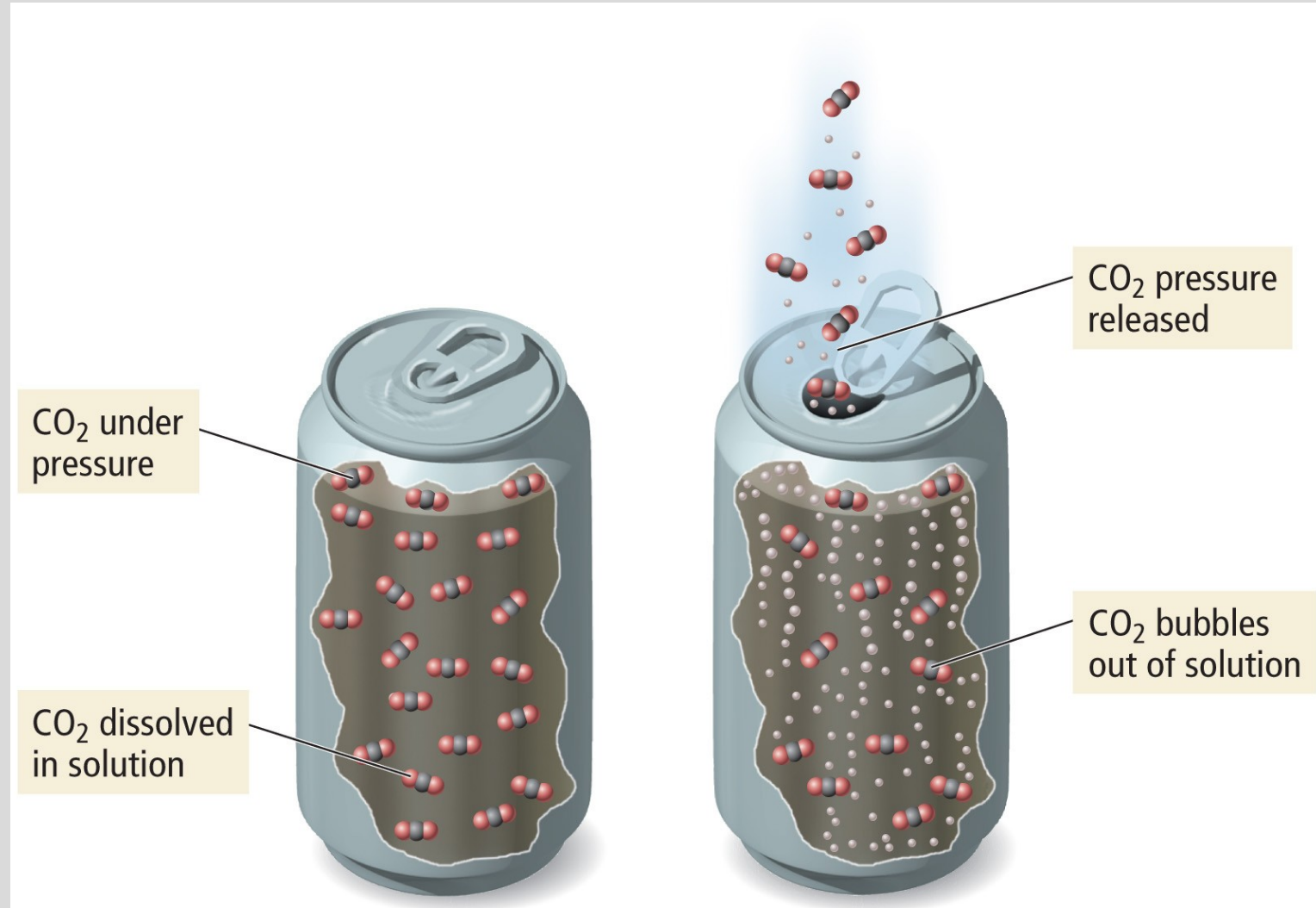
When **pressure is increased** by pushing on the piston, more gas particles are temporarily forced into solution than are able to leave.



Equilibrium restored

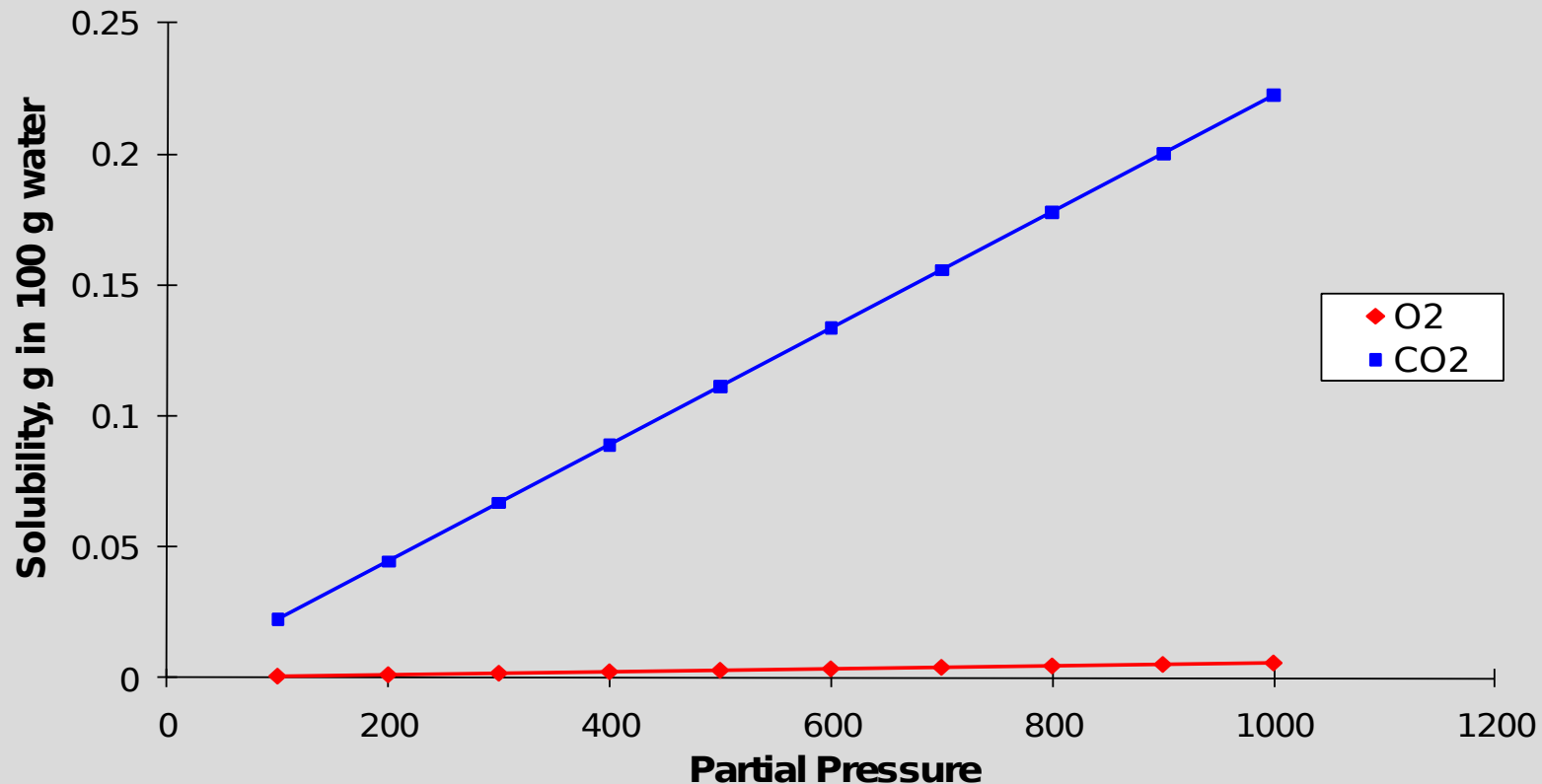
Solubility therefore increases until a **new equilibrium** is reached.

High pressure increases solubility, but when released, solubility is reduced.



Relationship between Partial Pressure and Solubility of a Gas

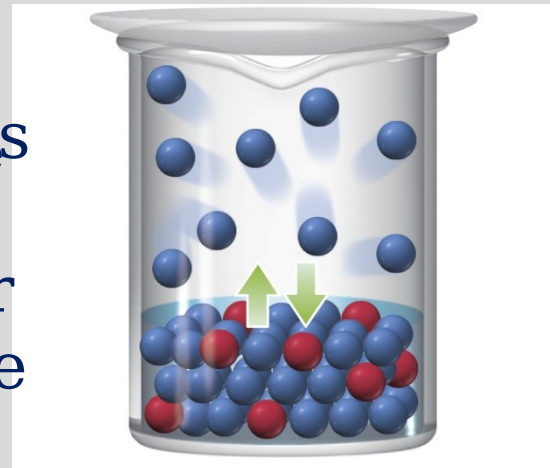
Solubility of Gases in Water at Various Pressures (temp = 20°C)



Vapor Pressure of Solutions

- the vapor pressure of a solvent above a solution is lower than the vapor pressure of the pure solvent
 - the solute particles replace some of the solvent molecules at the surface

Eventually, equilibrium is established between the liquid and vapor phases. The pure solvent has a higher rate of vaporization than the solution, so the rate of condensation must increase to reach equilibrium. This is achieved by decreasing the amount of solvent molecules in the vapor phase, thus lowering the vapor pressure.



Henry's Law

- the solubility of a gas (S_{gas}) is directly proportional to its partial pressure, (P_{gas})

$$S_{gas} = k_H P_{gas}$$

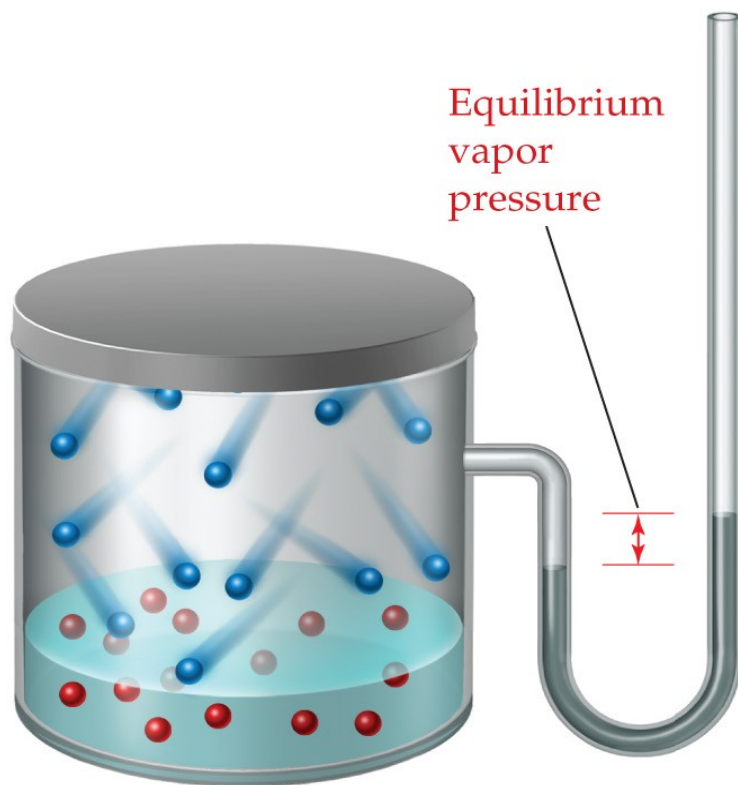
- k_H is called **Henry's Law Constant**

TABLE 12.4 Henry's Law Constants for Several Gases in Water at 25 °C

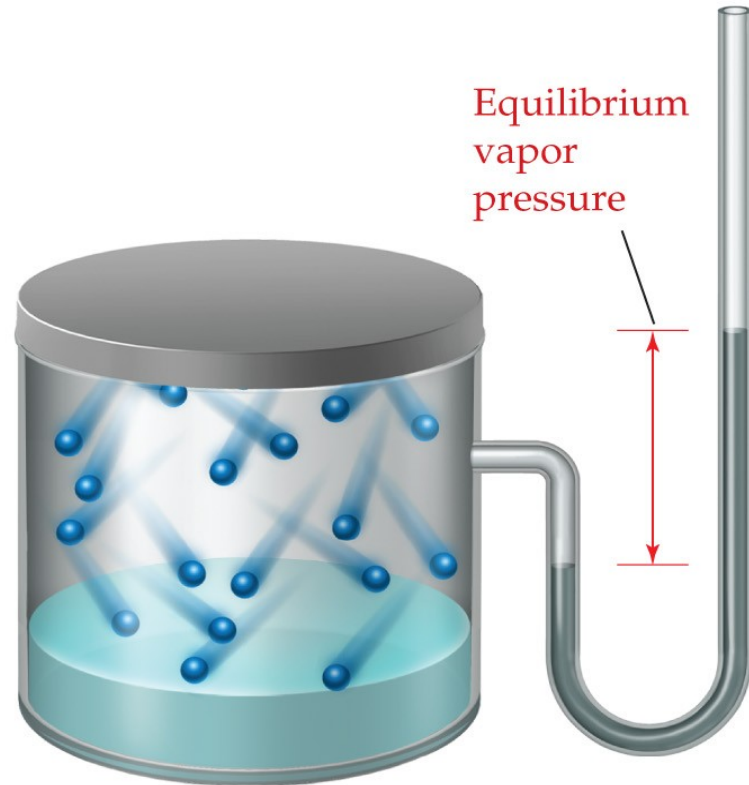
Gas	k_H (M/atm)
O ₂	1.3×10^{-3}
N ₂	6.1×10^{-4}
CO ₂	3.4×10^{-2}
NH ₃	5.8×10^1
He	3.7×10^{-4}

Vapor-Pressure Lowering of Solutions: Raoult's Law

$$\text{Raoult's Law } P_{\text{soln}} = P_{\text{solvent}} X_{\text{solvent}}$$



A solution of a **nonvolatile solute** always has a lower vapor pressure than ...



... that of the **pure solvent** by an amount that depends on the mole fraction of the solvent.

Raoult's Law for Volatile Solute

- when both the solvent and the solute can evaporate, both molecules will be found in the vapor phase
- the total vapor pressure above the solution will be the sum of the vapor pressures of the solute and solvent
 - for an ideal solution

$$P_{\text{total}} = P_{\text{solute}} + P_{\text{solvent}}$$

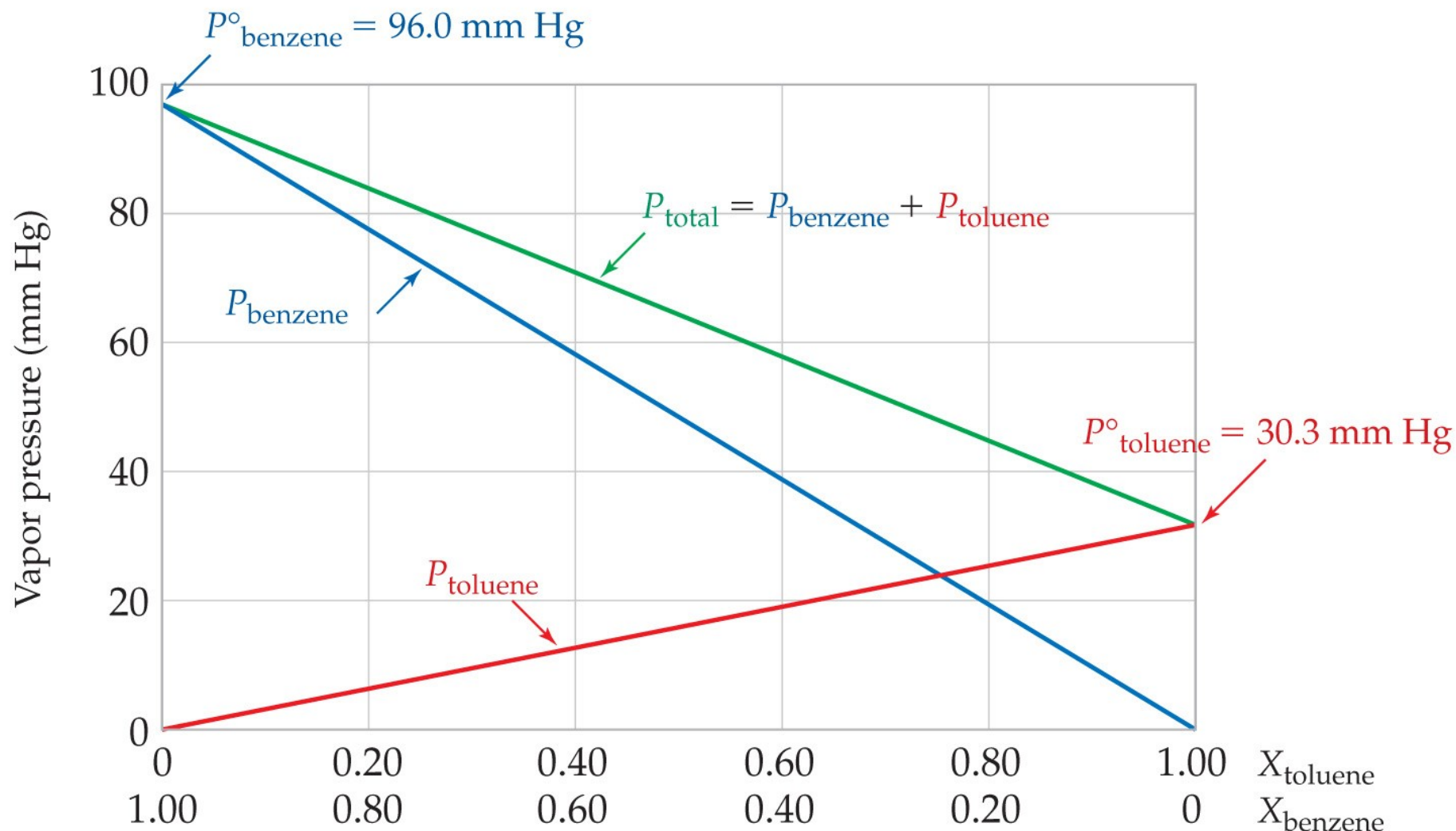
- the solvent decreases the solute vapor pressure in the same way the solute decreased the solvent's

$$P_{\text{solute}} = \chi_{\text{solute}} \cdot P^{\circ}_{\text{solute}} \quad \text{and} \quad P_{\text{solvent}} = \chi_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}}$$

Vapor-Pressure Lowering of Solutions:

Raoult's Law

$$P_{\text{total}} = P_A + P_B = (P_A^\circ X_A) + (P_B^\circ X_B)$$



Ionic Solutes and Vapor Pressure

- according to Raoult's Law, the effect of solute on the vapor pressure simply depends on the number of solute particles
- when ionic compounds dissolve in water, they dissociate – so the number of solute particles is a multiple of the number of moles of formula units
- the effect of ionic compounds on the vapor pressure of water is magnified by the dissociation
 - since NaCl dissociates into 2 ions, Na^+ and Cl^- , one mole of NaCl lowers the vapor pressure of water twice as much as 1 mole of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ molecules would

Effect of Ionic Dissociation

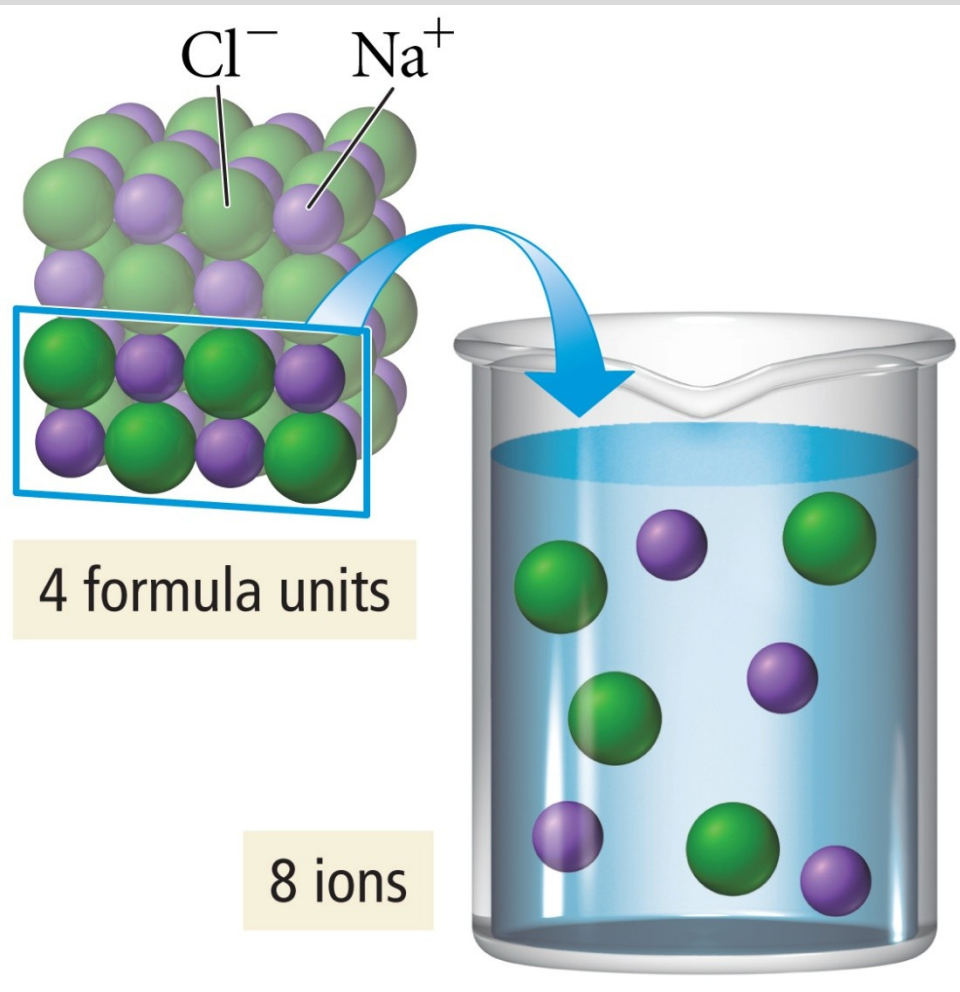


TABLE 12.9 Van't Hoff Factors at 0.05 *m* Concentration in Aqueous Solution

Solute	<i>i</i> Expected	<i>i</i> Measured
Nonelectrolyte	1	1
NaCl	2	1.9
MgSO_4	2	1.3
MgCl_2	3	2.7
K_2SO_4	3	2.6
FeCl_3	4	3.4

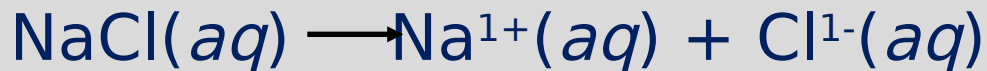
Vapor-Pressure Lowering of Solutions: Raoult's Law

Solutions of ionic substances often have a vapor pressure significantly lower than predicted, because the ion-dipole forces between the dissolved ions and polar water molecules are so strong.

van't Hoff Factor: $i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$

Vapor-Pressure Lowering of Solutions: Raoult's Law

van't Hoff Factor: $i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$



For sodium chloride, the predicted value of $i = 2$. For a 0.05 *m* (0.05 mol NaCl/1Kg solvent) solution of sodium chloride, the experimental value for $i = 1.9$ (one mol NaCl should give 2 mole ions)

Therefore, 1.9 mol = 1.8 mol Na⁺ and Cl⁻ and 0.1 mol NaCl per 1 mol NaCl to start.

0.1 mol NaCl is not dissolved, so it is 90% dissociated

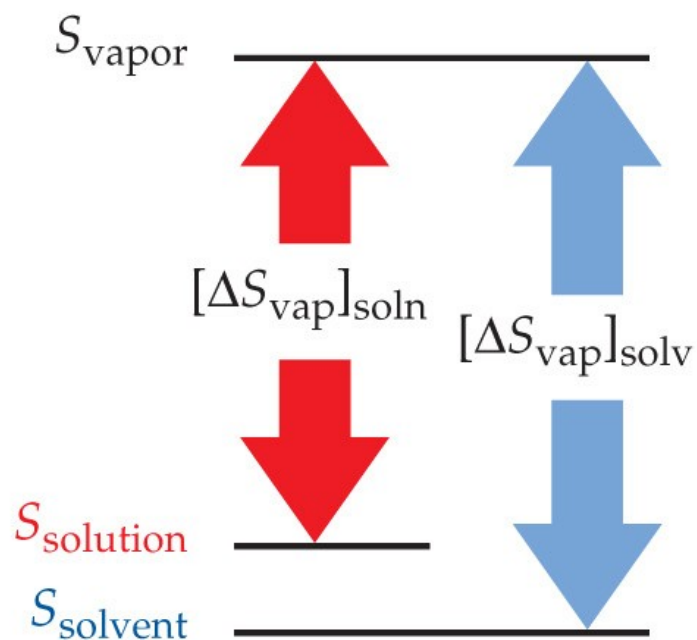
Vapor-Pressure Lowering of due to non-ionic, non- volatile solute: Raoult's Law

The vapor pressure of pure water at 25 °C is 23.76 mm Hg. What is the vapor pressure of a solution made from 1.00 mol glucose in 15.0 mol of water at 25 °C? Glucose is a nonvolatile solute.

$$P_{\text{soln}} = P_{\text{solvent}} X_{\text{solvent}}$$

$$= 23.76 \text{ mm Hg}_x \frac{15.0 \text{ mol}}{1.00 \text{ mol} + 15.0 \text{ mol}} = 22.3 \text{ mm Hg}$$

Because the entropy of the solvent in a solution is higher than that of pure solvent to begin with, ΔS_{vap} is smaller for the solution than for the pure solvent.



If this is similar for the solvent and the solution ...

... and this is smaller for the solution ...

$$\Delta H_{\text{vap}} - T\Delta S_{\text{vap}} = \Delta G_{\text{vap}}$$

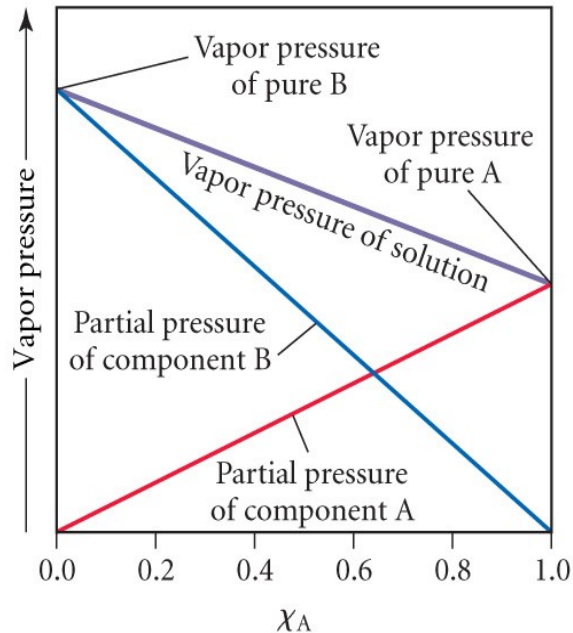
... then this is less negative for the solution.

As a result, vaporization of the solvent from the solution is less favored (less negative ΔG_{vap}), and the vapor pressure of the solution is lower.

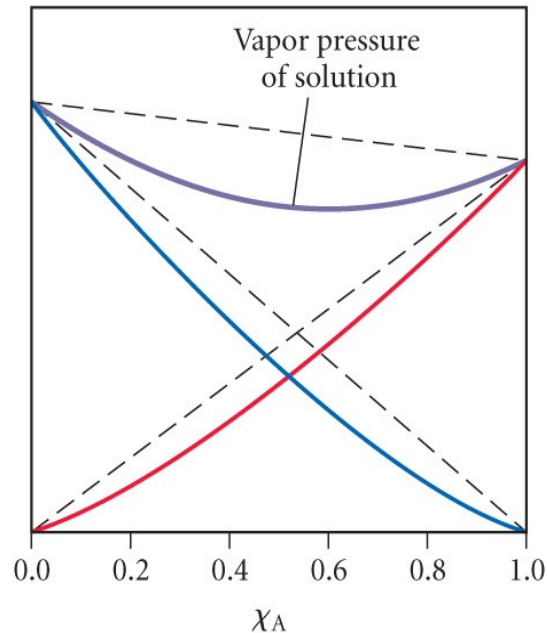
Deviations from Raoult's Law

Deviations from Raoult's Law

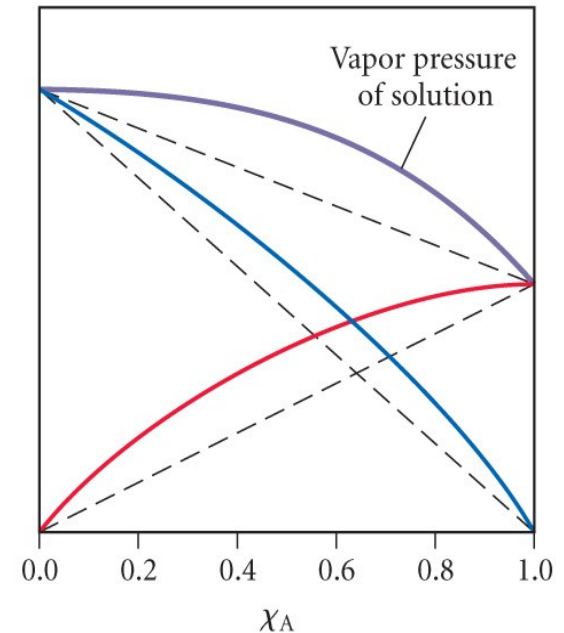
(a) Ideal solution



(b) Strong solute-solvent interactions

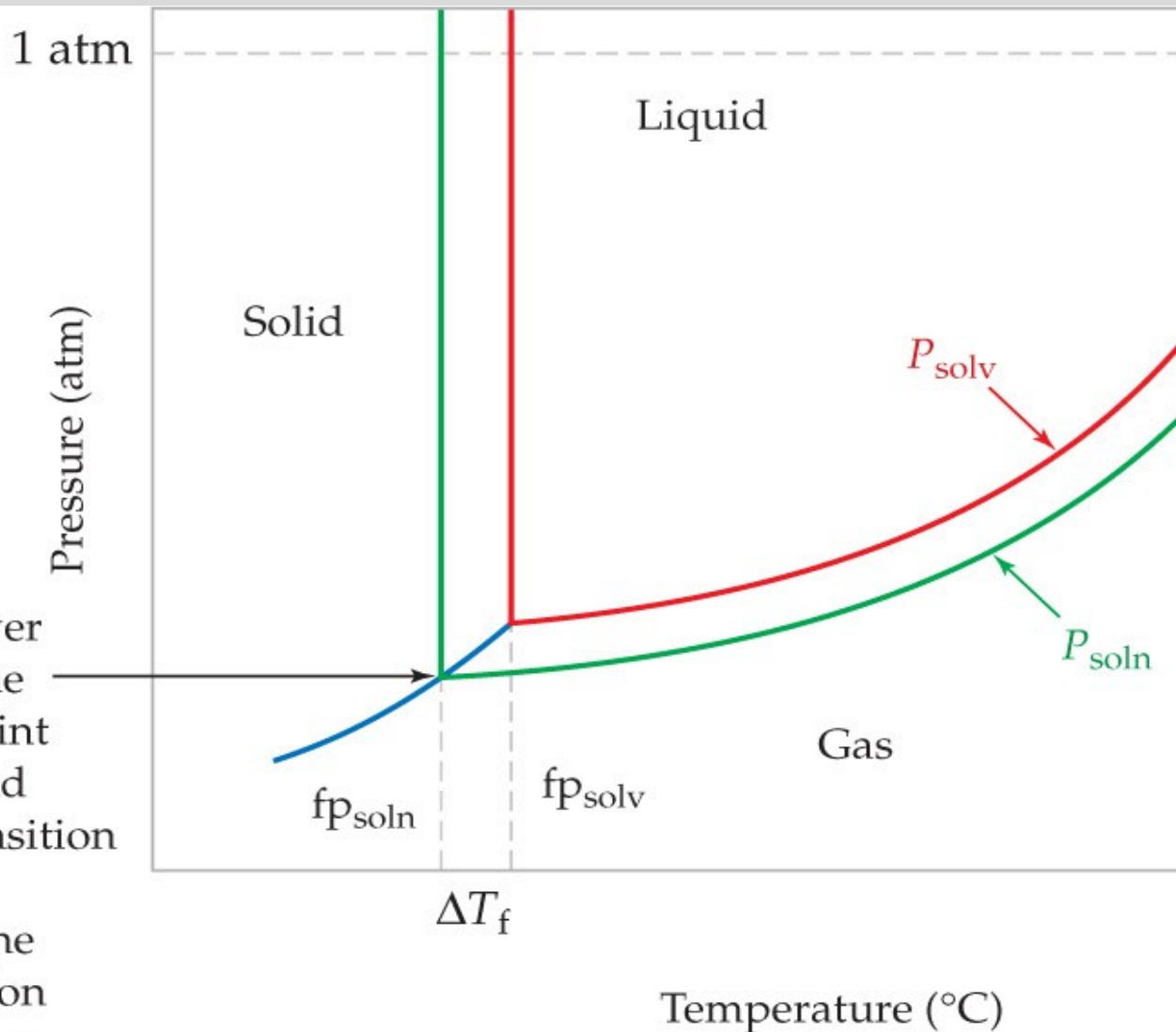


(c) Weak solute-solvent interactions

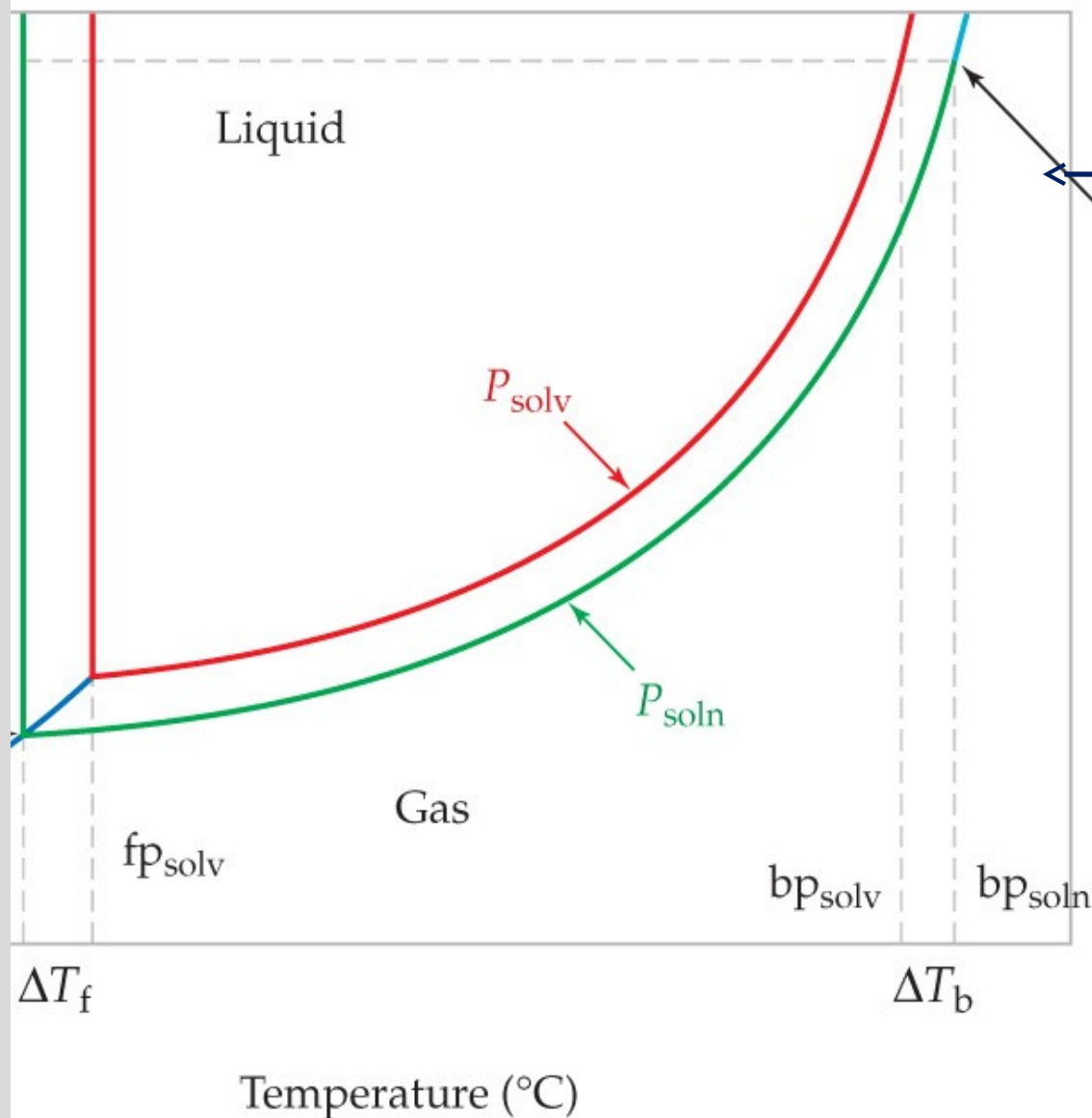


Freezing-Point Depression

Because the liquid/vapor phase transition line is lower for the **solution** than for the **pure solvent**, the triple-point temperature T_t is lower and the solid/liquid phase transition line is shifted to a lower temperature. As a result, the freezing point of the solution is lower than that of the pure solvent by an amount ΔT_f .



Boiling-Point Elevation



1 atm

Because the vapor pressure of the **solution** is lower than that of the **pure solvent** at a given temperature, the temperature at which the vapor pressure reaches atmospheric pressure is higher for the solution than for the solvent. Thus, the boiling point of the solution is higher by an amount ΔT_b .

Boiling-Point Elevation and Freezing-Point Depression

Nonelectrolytes

$$\Delta T_b = K_b m$$

$$\Delta T_f = K_f m$$

Electrolytes

$$\Delta T_b = K_b m i$$

$$\Delta T_f = K_f m i$$

m = molality

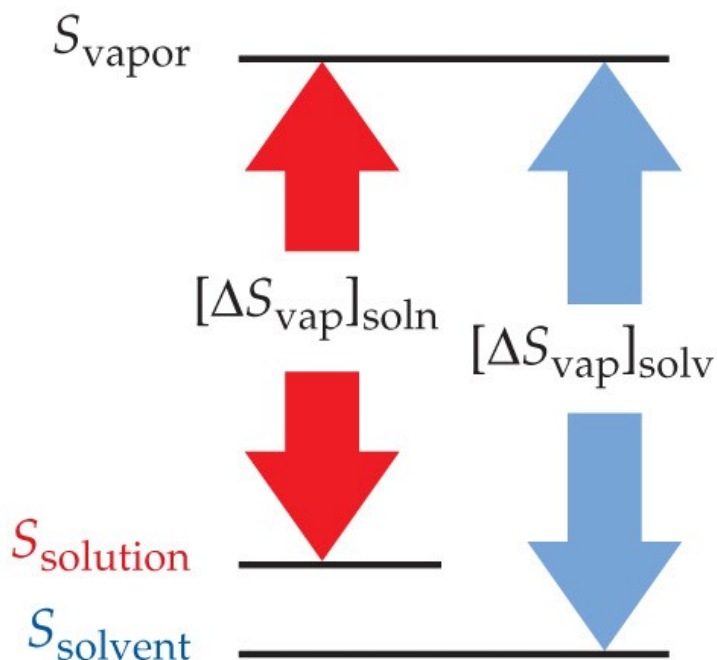
i = van't Hoff factor

Boiling-Point Elevation and Freezing-Point Depression

TABLE 11.4 Molal Boiling-Point-Elevation Constants (K_b) and Molal Freezing-Point-Depression Constants (K_f) for Some Common Substances

Substance	K_b [(°C · kg)/mol]	K_f [(°C · kg)/mol]
Benzene (C ₆ H ₆)	2.64	5.07
Camphor (C ₁₀ H ₁₆ O)	5.95	37.8
Chloroform (CHCl ₃)	3.63	4.70
Diethyl ether (C ₄ H ₁₀ O)	2.02	1.79
Ethyl alcohol (C ₂ H ₆ O)	1.22	1.99
Water (H ₂ O)	0.51	1.86

Because the solvent in a solution has a higher entropy to begin with, ΔS_{vap} is **smaller for the solution** than for the **pure solvent**.



If this is similar for the solvent and the solution ...

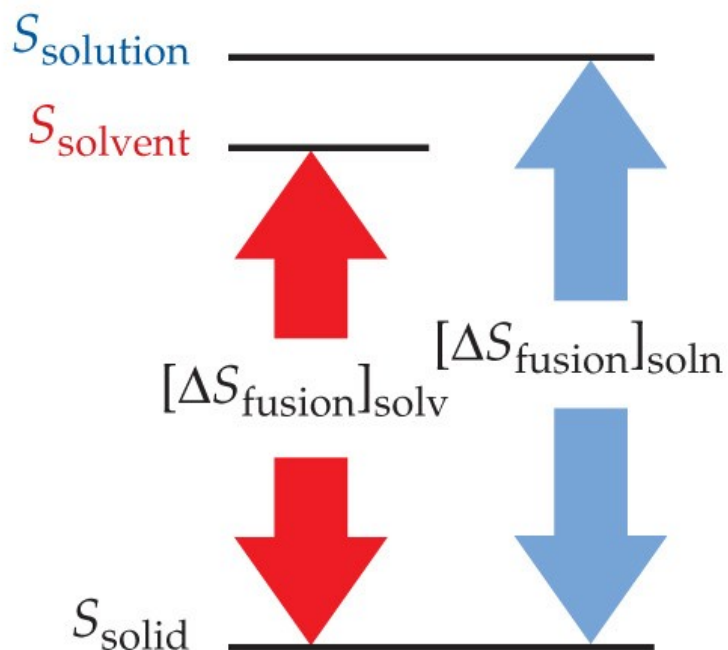
$$\frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = T_b$$

... and this is smaller for the solution, ...

... then this is larger for the solution.

As a result, the boiling point of the solution T_b is higher than that of the pure solvent.

Because the solvent in a solution has a higher entropy level to begin with, ΔS_{fusion} is larger for the solution than for the pure solvent.



If this is similar for the solvent and the solution ...

$$\frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}} = T_f$$

... and this is larger for the solution ...

... then this is smaller for the solution.

As a result, the freezing point of the solution T_f is lower than that of the pure solvent.

Boiling-Point Elevation and Freezing-Point Depression

What is the freezing point of a solution prepared by dissolving 7.40 g of MgCl_2 in 110 g of water? The van't Hoff factor for MgCl_2 is $i = 2.7$.

Calculate the moles of MgCl_2 :

$$7.40 \text{ g} \times \frac{1 \text{ mol}}{95.3 \text{ g}} = 0.0776 \text{ mol}$$

Calculate the molality of the solution:

$$\frac{0.0776 \text{ mol}}{110 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 0.71 \frac{\text{mol}}{\text{kg}}$$

Boiling-Point Elevation and Freezing-Point Depression

Calculate the freezing point of the solution:

$$\Delta T_f = K_f m i = 1.86 \frac{^{\circ}\text{C kg}}{\text{mol}} \times 0.71 \frac{\text{mol}}{\text{kg}} \times 2.7 = 3.6 ^{\circ}\text{C}$$

$$T_f = 0.0 ^{\circ}\text{C} - 3.6 ^{\circ}\text{C} = \boxed{-3.6 ^{\circ}\text{C}}$$

Osmosis and Osmotic Pressure

Osmosis: The passage of solvent through a semipermeable membrane from the less concentrated side to the more concentrated side.

Osmotic Pressure (π): The amount of pressure necessary to cause osmosis to stop.

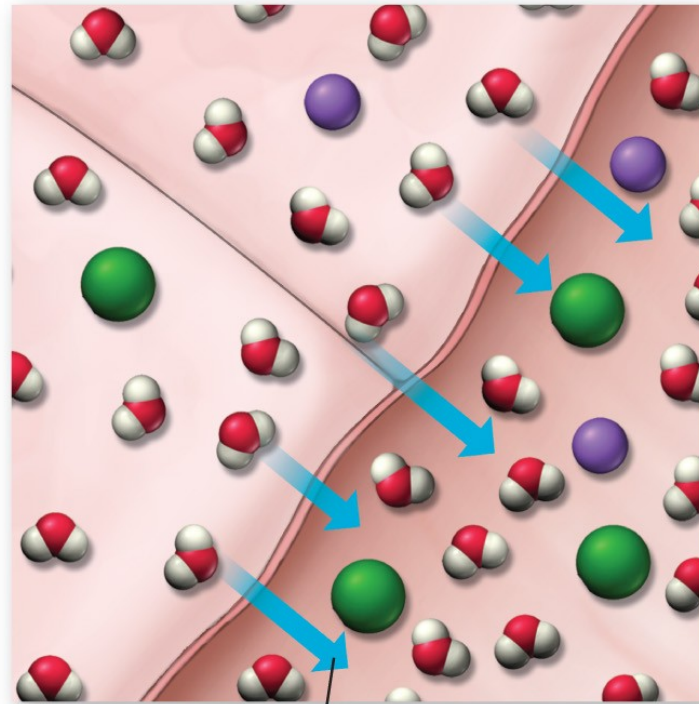
A cucumber shrivels into a pickle when immersed in salt water due to osmotic pressure.

Water moves out of the cucumber and into the salt solution to try to dilute the salt solution.

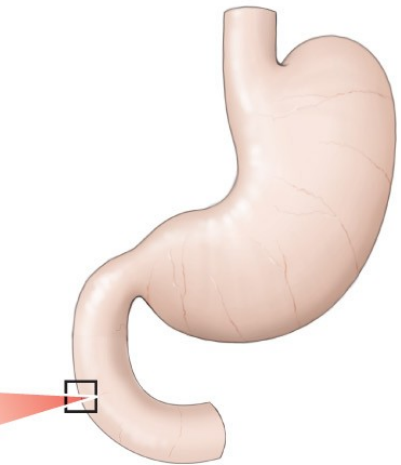


Ingesting Seawater

Interior of body cells
—dilute solution



Direction of water flow



Seawater in intestinal tract
—concentrated solution

Osmosis

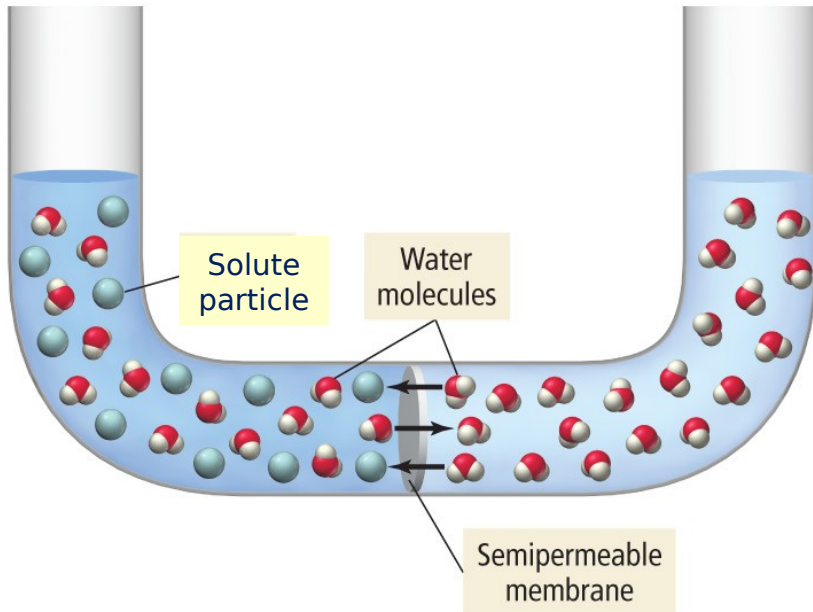
- **osmosis** is the flow of solvent through a semi-permeable membrane from solution of low concentration to solution of high concentration
- the amount of pressure needed to keep osmotic flow from taking place is called the **osmotic pressure**
- the osmotic pressure, Π , is directly proportional to the molarity of the solute particles

$$\Pi = MRT$$

$$R = 0.08206 \text{ (L}\cdot\text{atm)/(mol}\cdot\text{K)}$$

Osmosis and Osmotic Pressure

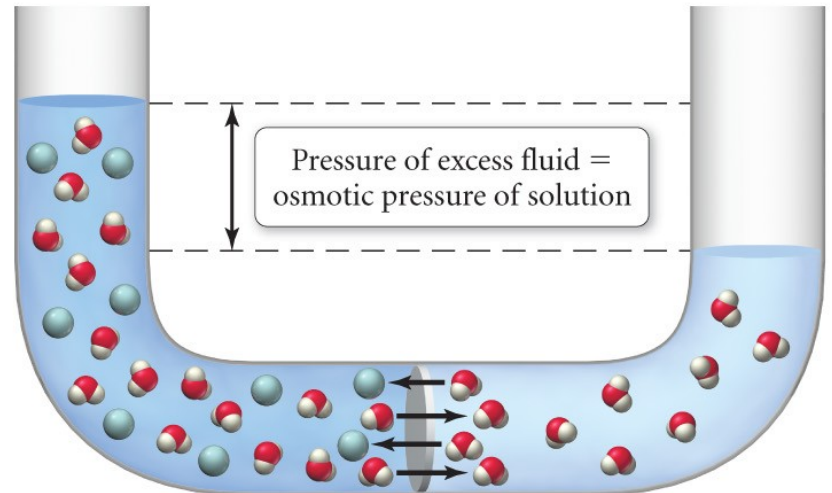
Initially



Water
level
rises



At equilibrium



Osmosis and Osmotic Pressure

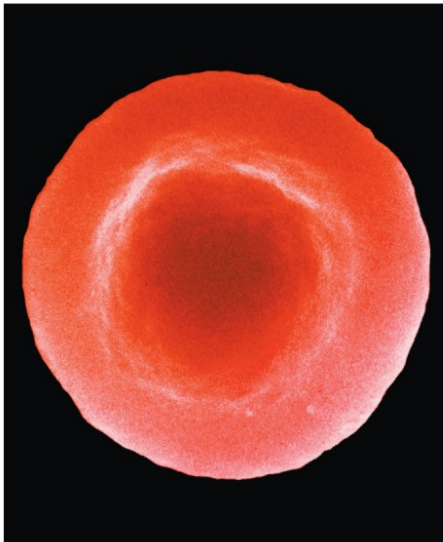
Calculate the osmotic pressure of a 1.00 M glucose solution in water at 300 K.

$$\Pi = MRT$$

$$= 1.00 \frac{\text{mol}}{\text{L}} \times 0.08206 \frac{\text{L atm}}{\text{K mol}} \times 300 \text{ K} = 24.6 \text{ atm}$$

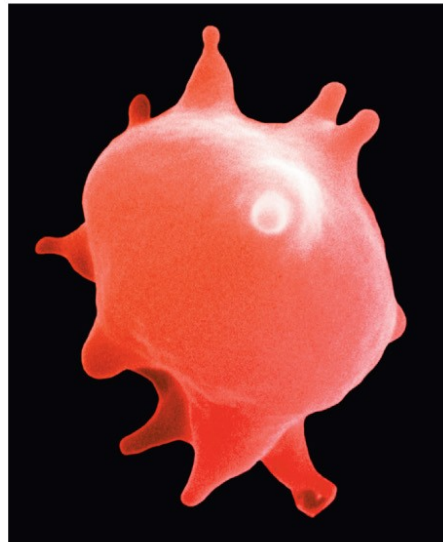
A hypertonic solution has a higher osmotic pressure than the solution inside the cell - as a result there is a net flow of water out of the cell, causing it to shrink.

Isosmotic
solution



(a) Normal red blood cell

Hyperosmotic
solution



(b) Shriveled red blood cell

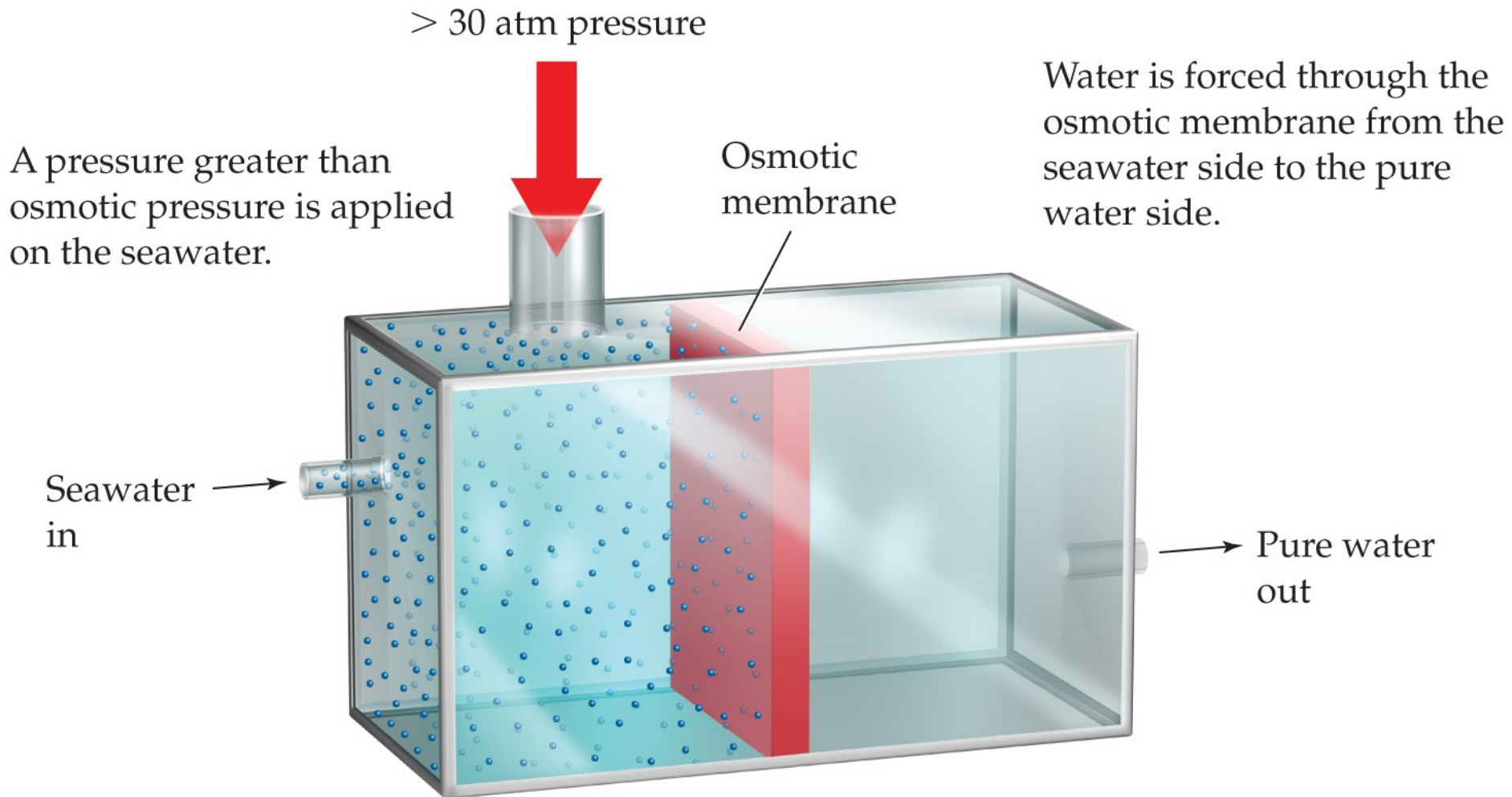
Hyposmotic
solution



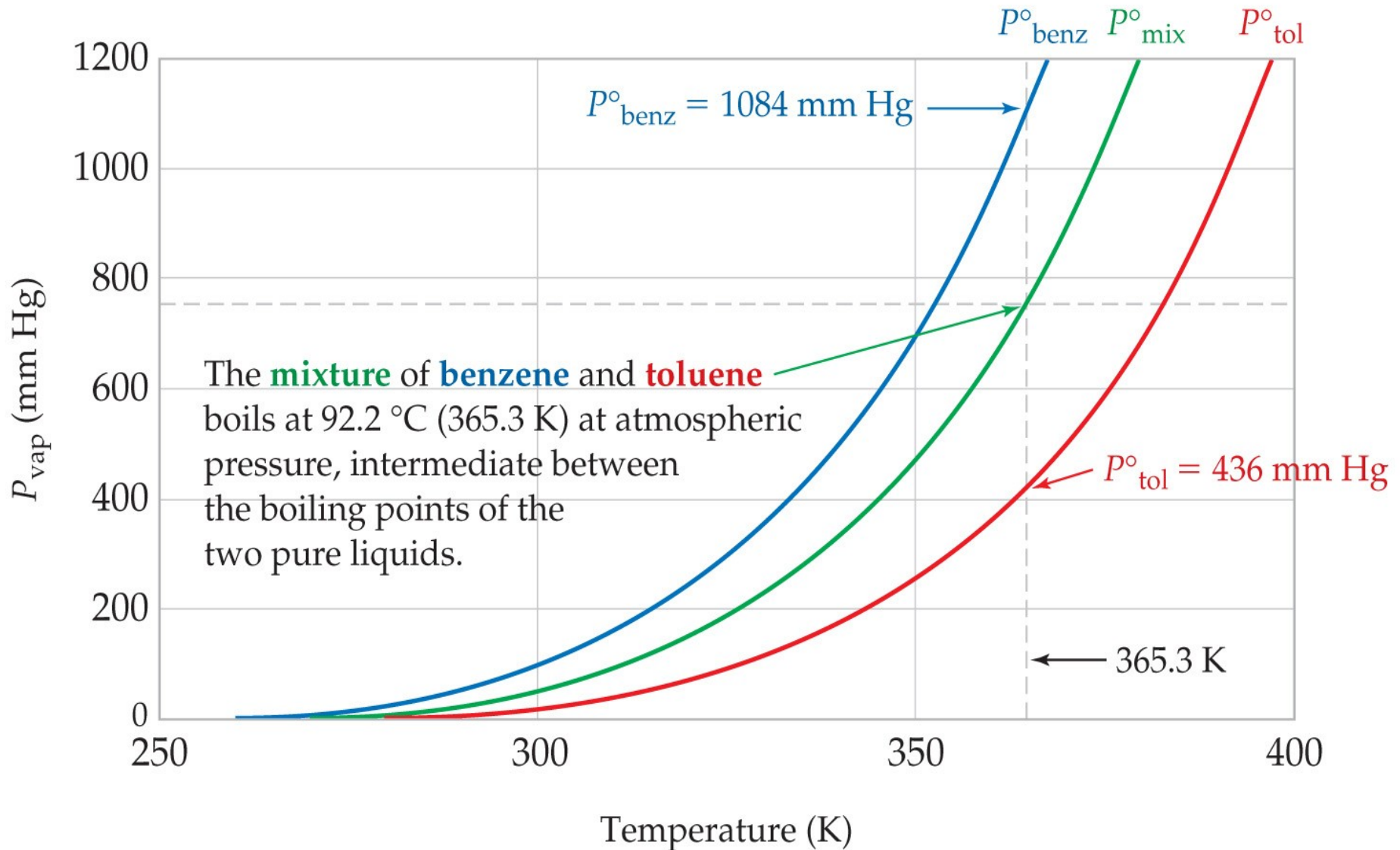
(c) Swollen red blood cell

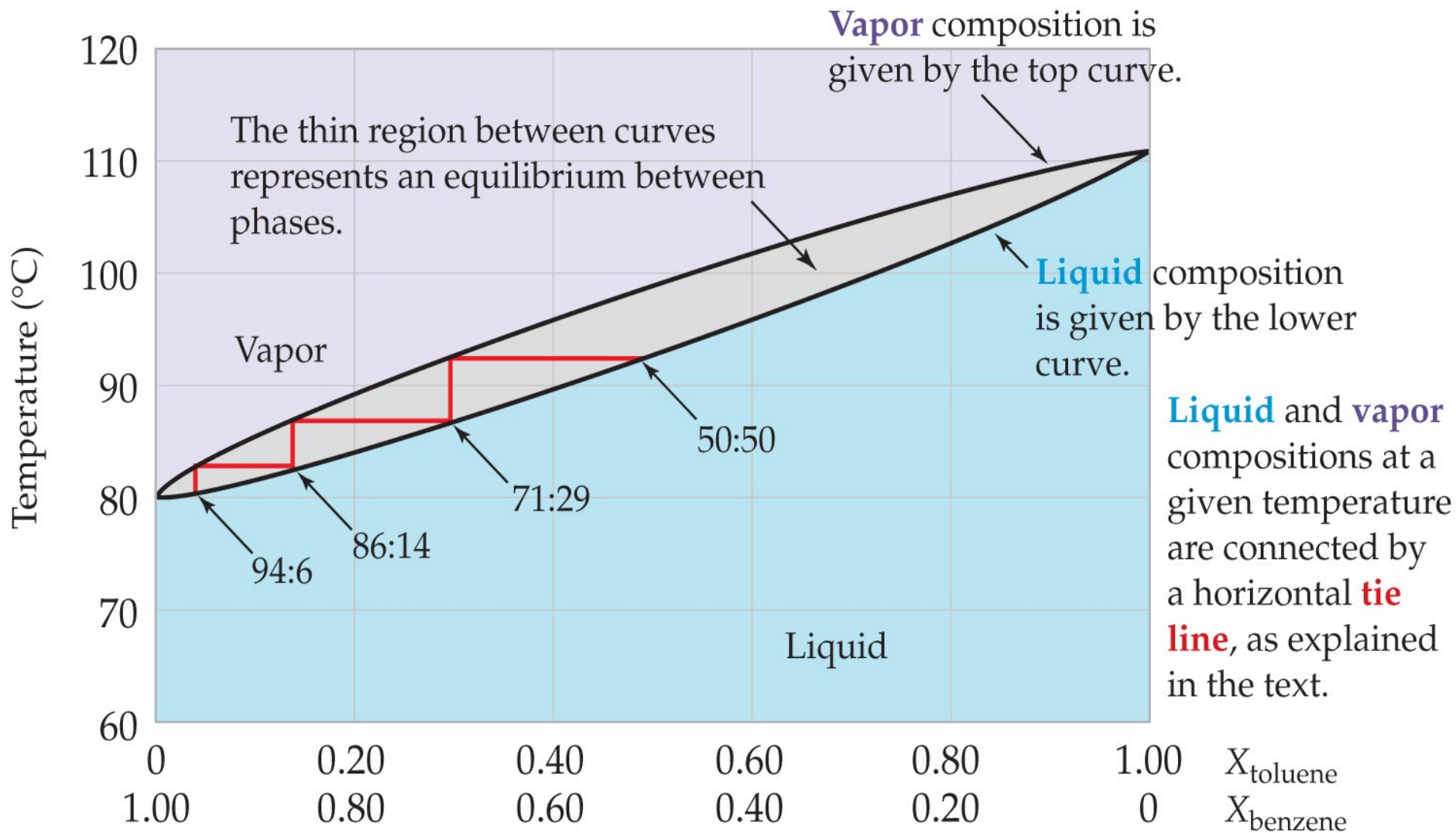
Some Uses of Colligative Properties

Reverse Osmosis



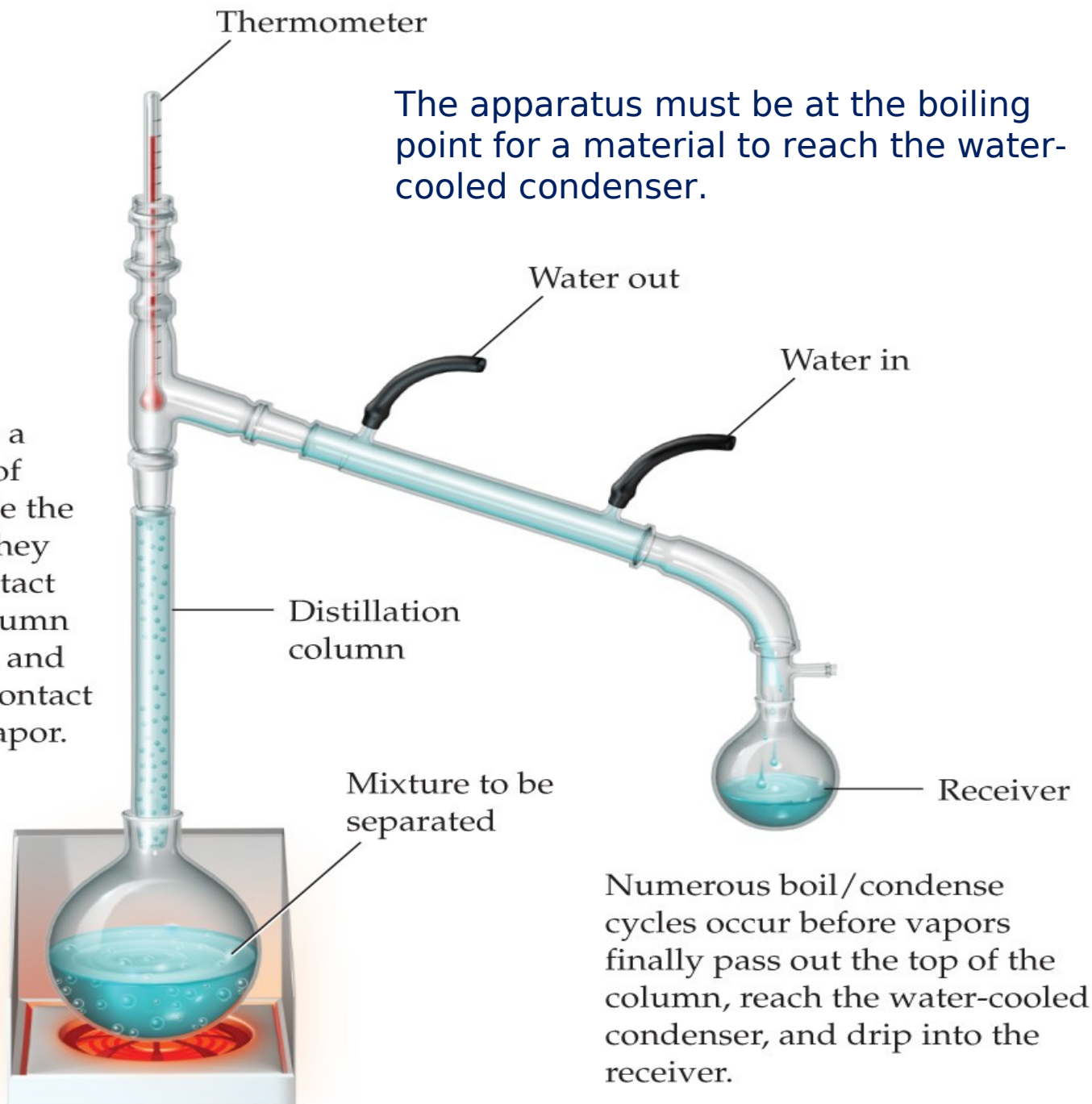
Fractional Distillation of Liquid





The apparatus must be at the boiling point for a material to reach the water-cooled condenser.

The vapors from a boiling mixture of liquids rise inside the column, where they condense on contact with the cool column walls, drip back, and are reboiled by contact with more hot vapor.

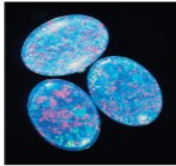


Numerous boil/condense cycles occur before vapors finally pass out the top of the column, reach the water-cooled condenser, and drip into the receiver.

Colloids

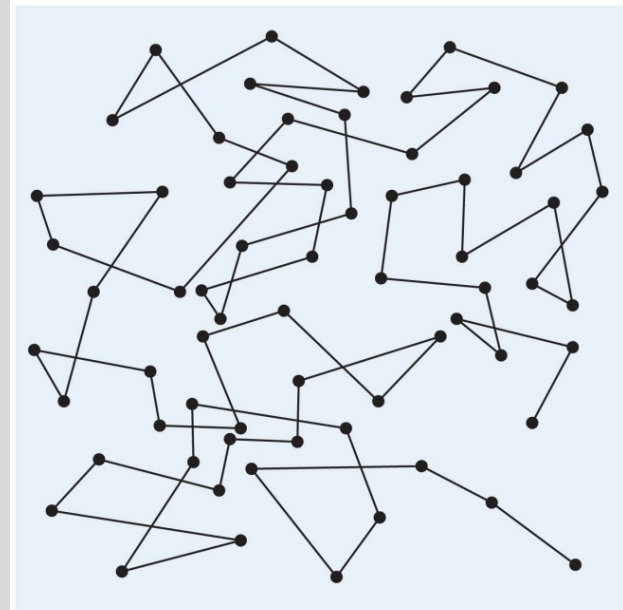
- a **colloidal suspension** is a heterogeneous mixture in which one substance is dispersed through another
 - most colloids are made of finely divided particles suspended in a medium
- the difference between colloids and regular suspensions is generally particle size – colloidal particles are from 1 to 100 nm in size

TABLE 12.10 Types of Colloidal Dispersions

Classification	Dispersing Substance (Solute-like)	Dispersing Medium (Solvent-like)	Example	
Aerosol	Liquid	Gas		Fog (water droplets in air)
Solid aerosol	Solid	Gas		Smoke (ash in air)
Foam	Gas	Liquid		Whipped cream (air bubbles in butterfat)
Emulsion	Liquid	Liquid		Milk (milk fat globules in water)
Solid emulsion	Liquid	Solid		Opal (water in silica glass)

Properties of Colloids

- the particles in a colloid exhibit **Brownian motion**



- colloids exhibit the **Tyndall Effect**
 - ✓ scattering of light as it passes through a suspension
 - ✓ colloids scatter short wavelength (blue) light more effectively than long wavelength (red) light



How would you prepare 250.0 g of 5.00% by mass glucose solution (normal glucose)?

Given: 250.0 g solution

Find: g Glucose

Equivalence: 5.00 g Glucose $\equiv$ 100 g solution

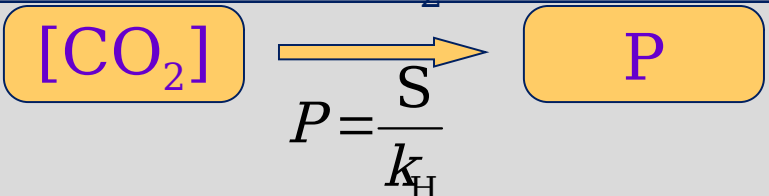
Solution Strategy: $\boxed{\text{g solution}} \xrightarrow{\frac{5.00 \text{ g Glucose}}{100 \text{ g solution}}} \boxed{\text{g Glucose}}$

Apply the Strategy:

$$250.0 \text{ g solution} \times \frac{5.00 \text{ g glucose}}{100 \text{ g solution}} = 12.5 \text{ g glucose}$$

Answer: Dissolve 12.5 g of glucose in enough water to total 250.0 g

What pressure of CO₂ is required to keep the [CO₂] = 0.12 M at 25°C?

Given:	$S = [\text{CO}_2] = 0.12 \text{ M},$
Find:	$P \text{ of CO}_2, \text{ atm}$
Concept Plan:	 $P = \frac{S}{k_H}$ $S = k_H P, k_H = 3.4 \times 10^{-2} \text{ M/atm}$
Relationships:	$P = \frac{S}{k_H} = \frac{0.12 \cancel{\text{M}}}{3.14 \times 10^2 \cancel{\text{M}} \cdot \text{atm}^{-1}} = 3.5 \text{ atm}$
Check:	the unit is correct, the pressure higher than 1 atm meets our expectation from general experience

What volume of 10.5% by mass soda contains 78.5 g of sugar?

Given:	78.5 g sugar, density sol'n = 1.04 g/mL
Find:	volume, mL
Concept Plan:	$\text{g solute} \xrightarrow{\frac{100\text{g sol'n}}{10.5\text{g sugar}}} \text{g sol'n} \xrightarrow{\frac{1\text{mL sol'n}}{1.04\text{g sol'n}}} \text{mL sol'n}$
Relationships:	100g sol'n = 10.5g sugar, density sol'n = 1.04 g/mL $78.5\text{g sugar} \times \frac{100\text{g}}{10.5\text{g sugar}} \times \frac{1\text{mL}}{1.04\text{g}} = 719\text{mL}$
Check:	the unit is correct, the magnitude seems reasonable as the mass of sugar $\approx 10\%$ the volume of solution

What is the molarity of a solution prepared by mixing 17.2 g of $\text{C}_2\text{H}_6\text{O}_2$ with 0.500 kg of H_2O to make 515 mL of solution?

Given:	17.2 g $\text{C}_2\text{H}_6\text{O}_2$, 0.500 kg H_2O , 515 mL
Find:	sol'n
Concept Plan:	$\text{g C}_2\text{H}_6\text{O}_2 \longrightarrow \text{mol C}_2\text{H}_6\text{O}_2 \quad M = \frac{\text{mol}}{\text{L}}$ $\text{mL sol'n} \longrightarrow \text{L sol'n} \quad M$ $M = \text{mol/L}$, 1 mol $\text{C}_2\text{H}_6\text{O}_2 = 62.07 \text{ g}$, 1 mL
Relationships:	$17.2 \text{ g C}_2\text{H}_6\text{O}_2 \times \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.07 \text{ g C}_2\text{H}_6\text{O}_2} = 0.2771 \text{ mol}$ $515 \text{ mL} \times \frac{0.001 \text{ L}}{1 \text{ mL}} = 0.515 \text{ L}$ $M = \frac{0.2771 \text{ mol C}_2\text{H}_6\text{O}_2}{0.515 \text{ L}}$ $M = 0.538 \text{ M}$
Check:	the unit is correct, the magnitude is reasonable

What is the molality of a solution prepared by mixing 17.2 g of $\text{C}_2\text{H}_6\text{O}_2$ with 0.500 kg of H_2O to make 515 mL of solution?

Given:	17.2 g $\text{C}_2\text{H}_6\text{O}_2$, 0.500 kg H_2O , 515 mL
Find:	sol'n
Concept Plan:	$\text{g C}_2\text{H}_6\text{O}_2 \longrightarrow \text{mol C}_2\text{H}_6\text{O}_2 \quad m = \frac{\text{mol}}{\text{kg}}$ kg H_2O m $m = \text{mol/kg}, 1 \text{ mol C}_2\text{H}_6\text{O}_2 = 62.07 \text{ g}$
Relationships:	$m = \frac{0.271 \text{ mol C}_2\text{H}_6\text{O}_2}{0.500 \text{ kg H}_2\text{O}}$ $m = 0.542 \text{ m}$ $17.2 \text{ g C}_2\text{H}_6\text{O}_2 \times \frac{1 \text{ mol C}_2\text{H}_6\text{O}_2}{62.07 \text{ g C}_2\text{H}_6\text{O}_2} = 0.271 \text{ mol}$
Check:	the unit is correct, the magnitude is reasonable

What is the percent by mass of a solution prepared by mixing 17.2 g of $\text{C}_2\text{H}_6\text{O}_2$ with 0.500 kg of H_2O to make 515 mL of solution?

Given:	17.2 g $\text{C}_2\text{H}_6\text{O}_2$, 0.500 kg H_2O , 515 mL
Find:	sol'n
Concept Plan:	$\frac{\text{g C}_2\text{H}_6\text{O}_2}{\text{g solvent}} \times 100\% = \frac{\text{g solute}}{\text{g sol'n}} \times 100\%$ g solvent → g sol'n %
Relationships:	$0.500 \text{ kg H}_2\text{O} \times \frac{1000 \text{ g H}_2\text{O}}{1 \text{ kg H}_2\text{O}} = 5.00 \times 10^2 \text{ g H}_2\text{O}$ $17.2 \text{ g C}_2\text{H}_6\text{O}_2 + 500 \text{ g H}_2\text{O} = 517.2 \text{ g sol'n}$
Solve!	$\% = \frac{17.2 \text{ g C}_2\text{H}_6\text{O}_2}{517.2 \text{ g sol'n}} \times 100\%$ $\% = 3.33\%$
Check:	the unit is correct, the magnitude is reasonable

What is the mole fraction of a solution prepared by mixing 17.2 g of $C_2H_6O_2$ with 0.500 kg of H_2O to make 515 mL of solution?

Given:	17.2 g $C_2H_6O_2$, 0.500 kg H_2O , 515 mL
Find:	sol'n
Concept Plan:	$ \begin{array}{l} \text{g } C_2H_6O_2 \longrightarrow \text{mol } C_2H_6O_2 \\ \text{g } H_2O \longrightarrow \text{mol } H_2O \end{array} $ $ \chi = \frac{\text{mol}_A}{\text{mol}_{\text{total}}} $ $ \chi = \text{mol}_A / \text{mol}_{\text{tot}}, 1 \text{ mol } C_2H_6O_2 = 62.07 \text{ g}, 1 \text{ mol } H_2O $
Relationships:	$ \begin{array}{l} 17.2 \text{ g } C_2H_6O_2 \times \frac{1 \text{ mol } C_2H_6O_2}{62.07 \text{ g } C_2H_6O_2} = 0.2771 \text{ mol} \\ 0.500 \text{ kg } H_2O \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 27.75 \text{ mol } H_2O \end{array} $
Check: the unit is correct, the magnitude is reasonable	$ \chi = \frac{0.2771 \text{ mol } C_2H_6O_2}{(0.2771 \text{ mol } C_2H_6O_2 + 27.75 \text{ mol } H_2O)} $ $ \chi = 9.89 \times 10^{-3} $

Calculate the vapor pressure of water in a solution prepared by mixing 99.5 g of $C_{12}H_{22}O_{11}$ with 300.0 mL of H_2O

Given:	99.5 g $C_{12}H_{22}O_{11}$, 300.0 mL H_2O
Find:	P_{H_2O}
Concept Plan:	$g\ C_{12}H_{22}O_{11} \longrightarrow mol\ C_{12}H_{22}O_{11} \quad \chi = \frac{mol_A}{mol_{total}} \quad P = \chi \cdot P^\circ$ $mL\ H_2O \longrightarrow g\ H_2O \longrightarrow mol\ H_2O \quad X_{H_2O} \longrightarrow P_{H_2O}$
Relationships:	$P^\circ_{H_2O} = 23.8\ \text{torr}, 1\ \text{mol}\ C_{12}H_{22}O_{11} = 342.30\ \text{g}, 1\ \text{mol}\ H_2O$
Solve:	$99.5\cancel{g}\ C_{12}H_{22}O_{11} \times \frac{1\cancel{mol}\ C_{12}H_{22}O_{11}}{342.30\cancel{g}\ C_{12}H_{22}O_{11}} = 0.2907\ \text{mol}\ C_{12}H_{22}O_{11}$ $300.0\cancel{mL}\ H_2O \times \frac{1.00\cancel{g}}{1\cancel{mL}} \times \frac{1\cancel{mol}\ H_2O}{18.02\cancel{g}\ H_2O} = 16.65\ \text{mol}\ H_2O$ $\chi = \frac{1665\cancel{mol}\ H_2O}{(0.2907\cancel{mol}\ C_{12}H_{22}O_{11} + 1665\cancel{mol}\ H_2O)} = 0.9828$

Calculate the vapor pressure of water in a solution prepared by mixing 99.5 g of $C_{12}H_{22}O_{11}$ with 300.0 mL of H_2O

Solve:

$$99.5 \cancel{\text{g } C_{12}H_{22}O_{11}} \times \frac{1 \cancel{\text{mol } C_{12}H_{22}O_{11}}}{342.3 \cancel{\text{g } C_{12}H_{22}O_{11}}} = 0.2907 \text{ mol } C_{12}H_{22}O_{11}$$

$$300.0 \cancel{\text{mL } H_2O} \times \frac{1.00 \cancel{\text{g}}}{1 \cancel{\text{mL}}} \times \frac{1 \text{ mol } H_2O}{18.02 \cancel{\text{g } H_2O}} = 16.65 \text{ mol } H_2O$$

$$\chi = \frac{16.65 \cancel{\text{mol } H_2O}}{(0.2907 \cancel{\text{mol } C_{12}H_{22}O_{11}} + 16.65 \cancel{\text{mol } H_2O})} = 0.9828$$

$$\chi = 0.9828$$

$$P_{H_2O} = \chi_{H_2O} \cdot P^{\circ}_{H_2O} = (0.9828)(238 \text{ torr})$$

$$P_{H_2O} = 23.4 \text{ torr}$$

What is the vapor pressure of H₂O when 0.102 mol Ca(NO₃)₂ is mixed with 0.927 mol H₂O @ 55°C?

Given:	0.102 mol Ca(NO ₃) ₂ , 0.927 mol H ₂ O, P° = 118.1 torr
Find:	
Concept Plan:	$\chi_{\text{H}_2\text{O}}, P^\circ_{\text{H}_2\text{O}} \xrightarrow{P \text{ of H}_2\text{O}} P_{\text{H}_2\text{O}}$ $P = \chi \cdot P^\circ$ $P = \chi \cdot P^\circ$
Relationships:	$\text{Ca(NO}_3)_2 \rightarrow \text{Ca}^{2+} + 2 \text{NO}_3^- \therefore 3(0.102 \text{ mol solute})$ $\chi_{\text{H}_2\text{O}} = \frac{0.927 \text{ mol H}_2\text{O}}{(3(0.102 \text{ mol solute}) + 0.927 \text{ mol H}_2\text{O})}$ $\chi_{\text{H}_2\text{O}} = 0.7518$ $P_{\text{H}_2\text{O}} = \chi_{\text{H}_2\text{O}} \cdot P^\circ_{\text{H}_2\text{O}} = (0.7518)(118.1 \text{ torr})$ $P_{\text{H}_2\text{O}} = 88.8 \text{ torr}$

Check the unit is correct, the pressure lower than the normal vapor pressure makes sense

What is the freezing point of a 1.7 m aqueous ethylene glycol solution, $C_2H_6O_2$?

Given:	1.7 m $C_2H_6O_2(aq)$
Find:	$T_f, ^\circ C$
Concept Plan:	$m \xrightarrow{\Delta T_f = m \cdot K_f} \Delta T_f$ $\Delta T_f = m \cdot K_f$, $K_f \text{ for } H_2O = 1.86 ^\circ C/m$, $FP_{H_2O} = 0.00 ^\circ C$
Relationships:	$\Delta T_f = m \cdot K_{f,H_2O}$ $= (1.7 m) \left(1.86 \frac{^\circ C}{m} \right)$ $\Delta T_f = 3.2 ^\circ C$
Solve:	$FP_{H_2O} - FP_{soln} = \Delta T_f$ $0.00 ^\circ C - FP_{soln} = 3.2 ^\circ C$ $FP_{soln} = - 3.2 ^\circ C$
Check:	the unit is correct, the freezing point lower than the normal freezing point makes sense

How many g of ethylene glycol, $C_2H_6O_2$, must be added to 1.0 kg H_2O to give a solution that boils at $105^\circ C$?

Given:	1.0 kg H_2O , $T_b = 105^\circ C$
Find:	mass $C_2H_6O_2$, g
Concept Plan:	$\Delta T_b \longrightarrow m$ $\Delta T_b = m \cdot K_b$ $kg\ H_2O \xrightarrow[m = \frac{m_{\text{solute}}}{m_{\text{solvent}}}]{} mol\ C_2H_6O_2 \xrightarrow[\frac{62.07\ g}{1\ mol}]{} g\ C_2H_6O_2$ $\Delta T_b = m \cdot K_b, K_b\ H_2O = 0.512^\circ C/m, BP_{H_2O} = 100.0^\circ C$
Relationships Solve:	$MM_{C_2H_6O_2} = 62.07\ g/mol$ $\Delta T_b = m \cdot K_b$ $(105 - 100^\circ C) = m(0.512 \frac{^\circ C}{m})$ $m = 9.77m$ ps: $1.0\ kg\ H_2O \times \frac{9.77\ mol\ C_2H_6O_2}{1.0\ kg\ H_2O} \times \frac{62.07\ g\ C_2H_6O_2}{1\ mol\ C_2H_6O_2} = 6.1 \times 10^2\ g\ C_2H_6O_2$

What is the molar mass of a protein if 5.87 mg per 10 mL gives an osmotic pressure of 2.45 torr at 25°C?

Given:	5.87 mg/10 mL, P = 2.45 torr, T = 25°C
Find:	molar mass, g/mol
Concept Plan:	$\Pi, T \xrightarrow{\Pi = MRT} M$ $mL \xrightarrow{\frac{0.001 L}{1 mL}} L \xrightarrow{mol = M \times L} \text{mol protein}$ $\Pi = MRT, T(K) = T(^{\circ}C) + 273.15, R = 0.08206 \text{ atm} \cdot L / \text{mol} \cdot K$
Relationships:	$T(K) = T(^{\circ}C) + 273.15$ $= 25 + 273.15 = 298 K$ $M = \frac{\Pi}{RT}$ $M = \frac{2.45 \text{ torr}}{0.08206 \frac{\text{atm} \cdot L}{\text{mol} \cdot K} \cdot 298 K}$ $M = 1.318 \times 10^{-4} M$ $MM = \frac{5.87 \times 10^{-3} g}{1.318 \times 10^{-6} mol} = 4.45 \times 10^6 g/mol$
Solve:	$MM = \frac{5.87 \times 10^{-3} g}{1.318 \times 10^{-6} mol} = 4.45 \times 10^6 g/mol$

Note: 1.318×10^{-4} mol protein